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Synthesis and characterization of metallic materials for membrane technology

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ABSTRACT

Powder of metallic materials composed of Fe, Ni was proposed for membrane applications such as microfiltration devices. The powder was synthesized using thermal route of simultaneously sintering–reduction techniques. The resulting powder has specific porous structure and can be deposited on steel substrate. The formed phases were identified by X-ray phase analysis. The produced powder was characterized by reflected light microscope and scanning electron microscope along with energy-dispersive X-ray spectroscopy (EDX). The reduction behavior of metal oxides was followed up by thermogravimetric techniques. The kinetics data obtained from reduction process were used to elucidate the reduction mechanism under isothermal condition. The microstructure changes accompanying sintering–reduction processes were investigated under different experimental parameters such as temperature, holding time and gas composition. The results show that pure $Fe_{0.64}Ni_{0.36}$ with relatively high porosity can be fabricated via reduction route. The presence of NiO plays a significant role in the reduction of iron oxide as well as in the structural changes accompanying the reduction processes. The particle size distribution of the produced metallic materials is being controlled under the different operation conditions to get a homogenous porous metallic structure with well defined porosity. The main advantage of using porous ferroalloy materials is their narrow size distribution leading to a well defined pore size distribution after sintering and reduction.

1. Introduction

The filtration devices such as microfiltration are successfully used in the separation and concentration of particulate suspensions or solutions, the recovery of low molecular weight substances and, in some instances, the recovery of macromolecules such as proteins (Katiyar et al., 2004). Generally, microfiltration membranes can be classified into

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organic membranes which mainly made of polymeric compounds and inorganic membranes that contain ceramic or metallic materials. Inorganic microfiltration membranes can be operated at elevated temperatures, metal membranes are stable at temperatures ranging from 500 to 800 °C and many ceramic membranes are usable at over 1000 °C. The development of inorganic membranes for industrial applications enables the realization of high thermal capability, high chemical stability and good cleaning ability by means of high pressure or back flushing, which cannot be implemented by polymer membranes (Zaho et al., 2004).

Fabrication of inorganic membranes was studied by many investigators from different viewpoints (Keizer and Burggraaf, 1988; Cheryan, 1998; Hsieh et al., 1998; Ames et al., 2003; Lee et al., 2007). Meulenberg et al. (2006) developed porous composite membrane for filtration devices consisting of a ceramic TiO_2 membrane with pores in the range of 100 nm deposited on a thin planer metallic substrate made of 316 L stainless steel. The steel substrate is produced by tap casting while TiO_2 membrane was prepared by wet powder spraying and screen printing. It was found that the sintering temperature determined the properties of the ceramic membrane.

The present study introduces a new approach for manufacturing of porous metallic membrane via reduction of metal oxides. The formation of metallic materials with small pores could be achieved in two ways; when small particles of metal oxides are used as starting materials (average particle size 300–500 nm), metallic materials with pores less than 100 nm can be produced. The second way to achieve metallic materials with very small pores comes from the mechanism of reduction reactions of metal oxides where the removal of oxygen during reduction will enhance the formation of additional small pores.

The reduction route is a simple and economic route for producing ferroalloys such as Fe–Ni and Fe–Ni–Cr alloys. The composition of these alloys is often a key element to control the mechanical, chemical and physical properties of the synthesized alloys. The reduction phenomena of iron oxides doped metal oxides has been extensively studied using H_2, CO, H_2/CO gas mixtures and even with solid carbon under isothermal or non-isothermal conditions (Bryk and Lu, 1986; Nasr et al., 1995; Abdel Halim, 2007; Pineau et al., 2007; Abdel Halim et al., 2008). It was reported that the reduction processes of iron oxides doped metal oxides include many complicated reactions and take place in a stepwise manner via formation of a series of intermediate oxides and metal ferrites. Simultaneous sintering–reduction technique is a promising route for fabrication and optimization of microstructures of ferroalloy materials (Fe-M alloys).

However, in the present work, a graded metallic membrane composed of Fe, Ni and Cr was developed for microfiltration devices via novel route of simultaneously sintering–reduction techniques. The particle size distribution of the produced metallic materials is being controlled under the different operation conditions to get a homogenous porous metallic structure with well defined porosity. The main advantage of using porous ferroalloy materials is their narrow particle size distribution leading to a well defined pore size distribution after sintering and reduction. Such kind of metallic materials also seem to be promising for integration into advanced systems concepts for the production of liquid energy carriers and chemicals, separation of particles from fluids, oxygen

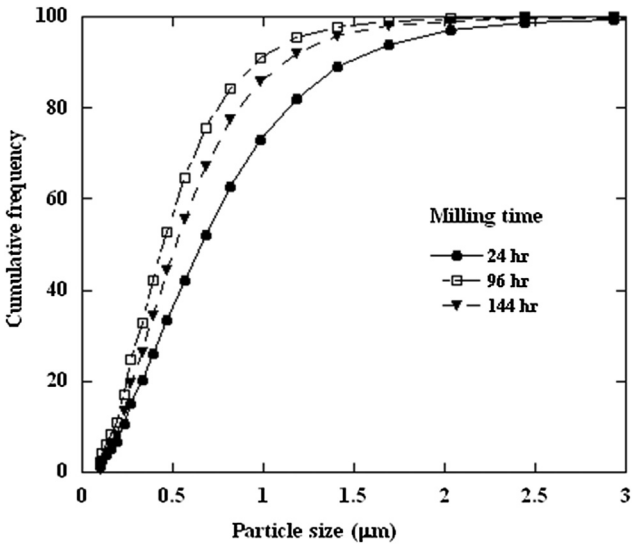

Fig. 1 – Effect of ball milling time on the particle size distribution of NiO powder.

Table 1 – Particle size measurements of starting powders after ball milling tests.

Powder	Time	Particle size, μm		
		d10	d50	d90
Fe_2O_3	0	0.29	0.85	2.05
	24	0.33	1.04	2.11
	96	0.25	0.81	1.67
	144	0.34	1.05	2.06
NiO	0	0.24	0.86	2.93
	24	0.24	0.66	1.46
	96	0.19	0.48	1.00
	144	0.22	0.53	1.11

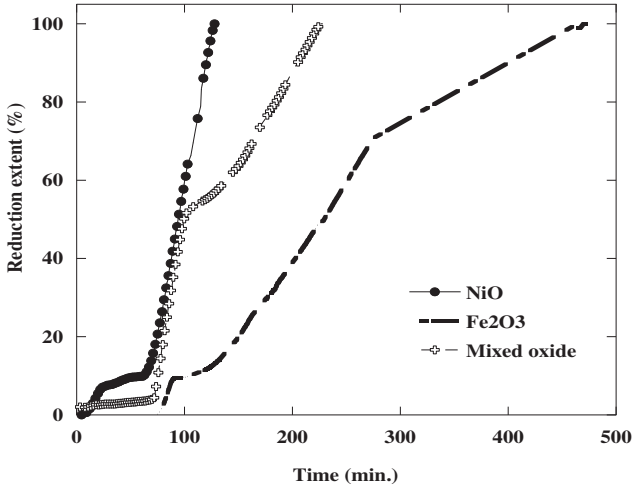

Fig. 2 – Non-isothermal reduction behavior of the starting powder materials.

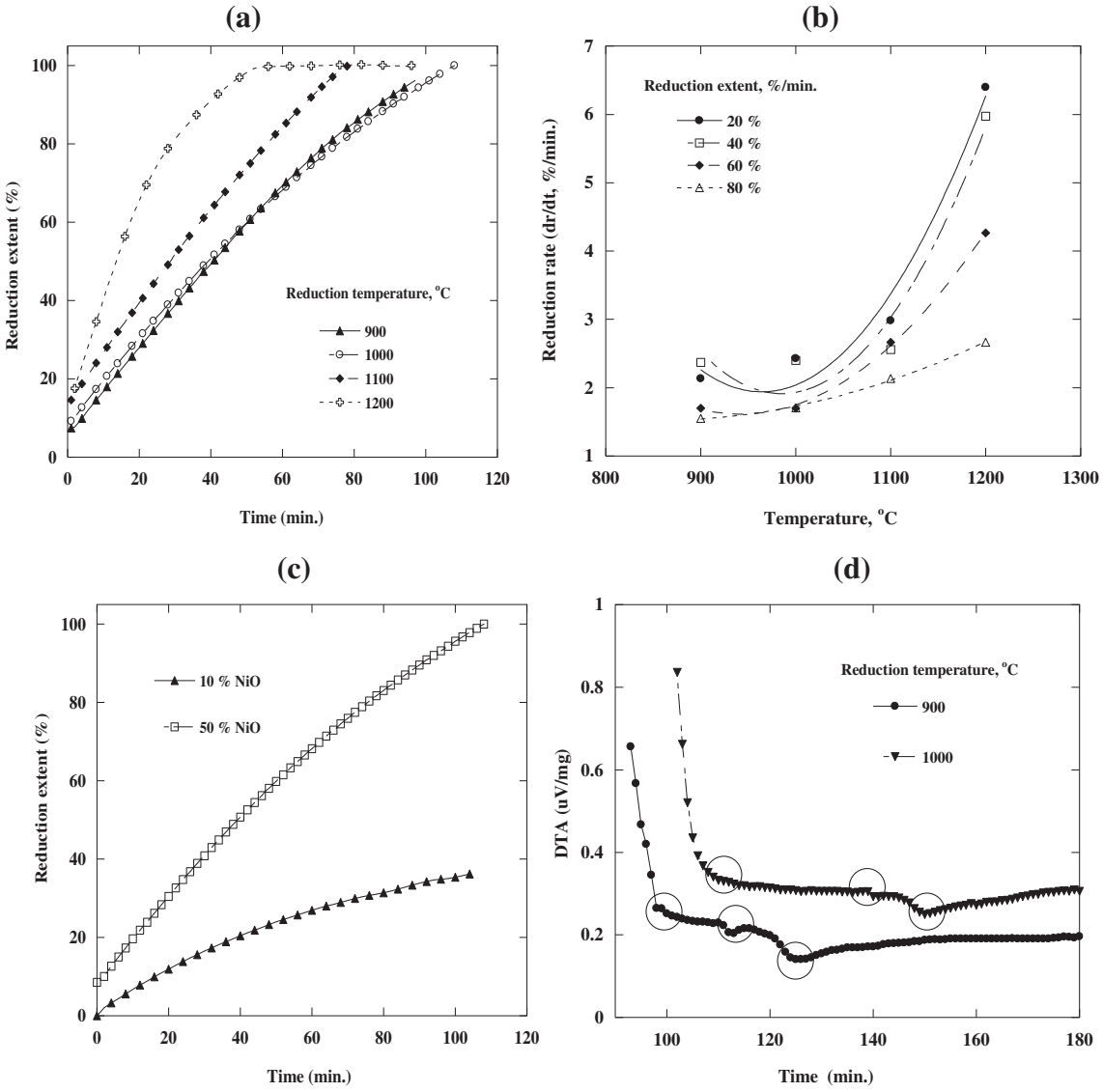

Fig. 3 – Reduction characteristics of Fe_2O_3–NiO mixtures at different reduction temperatures: (a) Typical reduction curves of 50 wt% NiO compacts. (b) Typical reduction rate at different stages 50 wt% NiO compacts. (c) Effect of NiO on the reducibility of Fe_2O_3. (d) DTA variation with time for Fe_2O_3 mixed with 50 wt% NiO compacts.

generation, low-CO_2-emission power generation and hydrogen technology (Mansur et al., 2004).

2. Materials and methods

A reagent grade iron oxide (III) powder (>=99%, Sigma–Aldrich Company, Germany) and NiO powder (99%, J.T. Baker Company, USA) were used as starting materials together with steel dense substrate (Crofer 22 Apu-1.4760). Both iron oxide and nickel oxide powders were separately subjected to ball milling process using zirconium dioxide balls and ethanol to get the powder with minimum particle size distribution. Different composite mixtures of iron oxide and nickel oxides were prepared. The prepared mixtures contain different weight percent of NiO (10 wt%, 25 wt% and 50 wt% NiO). The mixtures powders were strongly mixed in mortar agate and ball milled again for 2 h to ensure the complete homogeneity of the mixture.

Screen printing technique was used for the deposition of the mixed powder of Fe_2O_3 doped NiO on the steel substrate layer. A synthesized paste composed of mixed powder and binder composed of terpinol with 6% ethylcellulose was used for screen printing. The paste was homogenized on the three-roller mill. Printing of the paste on the stainless steel substrate was performed on a manual screen printing with 70 meshes/inch and Ø 0.065 mm. The distance between each mesh was 300 μm, a theoretical past thickness of 22 μm and an open screen area of 68%. The contact distance between sample and mesh was 2.0 mm. After drying the printed samples at 60 °C overnight, the samples were debindered at 400 °C for 1 h under Ar atmosphere. The samples were then reduced and sintered in one run at different temperatures and times in pure H_2 gas.

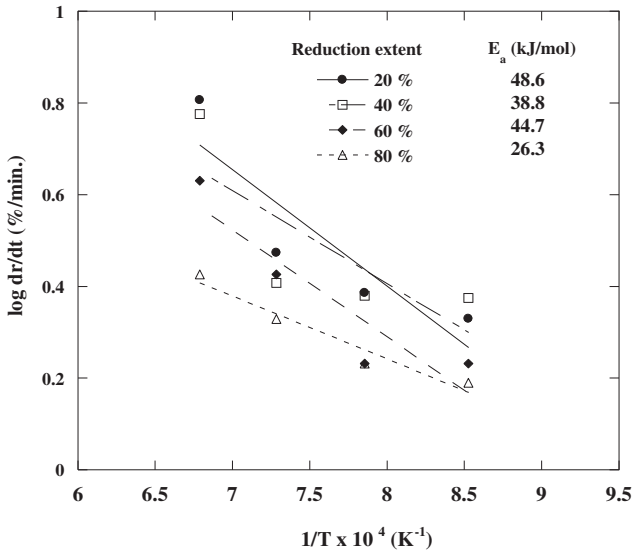

Fig. 4 – Arrhenius plots for reduction of mixed oxides (50 wt%) at different reduction extents.

The reducibility of the starting powder was investigated by thermogravimetric techniques DTA-TGA. For reduction experiments, iron oxide doped with different ratio of nickel oxide powders were compacted into tablets of 1 g weight, 10 mm diameter and 4 mm height. The reduction behavior of briquette samples was followed in the temperature range 900–1200 °C under pure Ar–4% H_2 at a flow rate 300 ml/min and 10 K/min heating rate. In another experiment, the prepared briquettes were subjected to sintering–reduction process in a horizontal tube furnace at 1000 °C for 10 h using Ar–4% H_2 gas to investigate the morphology and structural changes accompanying sintering–reduction processes.

The starting materials, reduced briquettes and the produced membranes were characterized by scanning electron microscope along with energy-dispersive X-ray spectroscopy (EDX) in order to investigate the microstructure with a LEO 1530 (Gemini) microscope. The phase identification was performed in a Siemens D-500 X-ray diffractometer with CuK_α radiation.

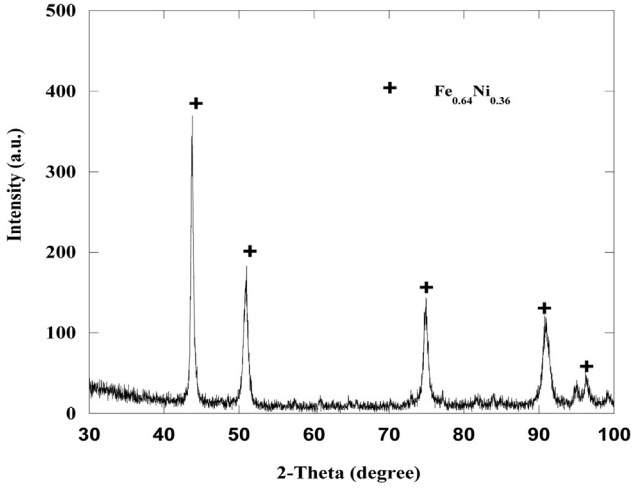

Fig. 5 – XRD analysis of iron oxide and 50 wt% NiO compact after sintering–reduction test.

Table 2 – The results of chemical analysis and porosity measurements of the produced ferroalloy.

Type	Fe, %	Ni, %	% Porosity
10% NiO	85.2	13.2	26
50% NiO	47.3	53.1	13

3. Results and discussion

3.1. *Reduction characteristics of starting materials*

The iron oxide and nickel oxide powders were subjected to ball milling process using ZrO_2 balls and ethanol to ensure that the starting powder has possible minimum particle size distribution. Table 1 shows the results of particle size distribution after 24, 96 and 144 h. The results show that ball milling has insignificant effect on the particle size distribution of iron oxide while nickel oxide powder was greatly affected by ball milling. The average variation of particle size (d50) of the powder was decreased from 800 nm to 500 nm as shown in Fig. 1.

The reducibility of the starting powder materials plays an important role in the fabrication of ferroalloys from metal oxides. The composition of the starting mixed oxide and reduction temperature are the main parameters controlling the reducibility of metal oxides. The general reduction behavior of both powders as well as mixture of them was investigated non-isothermally and isothermally using thermogravimetric technique. The course of reduction was followed up by measuring oxygen weight loss as a function of time in the temperature range of 900–1200 °C. The influence of reduction conditions and composition of starting materials on the reduction behavior and structural characteristics of the reduced products was studied in order to test the successful fabrication of ferroalloy of iron and nickel using gaseous reduction route. The reduction behavior of the starting materials is used to elucidate the kinetics and mechanisms of reduction process.

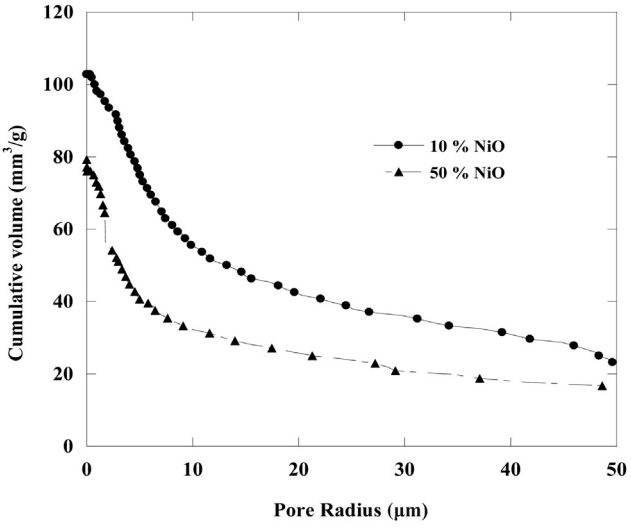

Fig. 6 – Influence of NiO content on the pore size distribution of the reduced powder.

First, the reduction characteristics of the starting powder Fe_2O_3, NiO and iron oxide doped 50% NiO was tested separately to ensure the complete reducibility of the starting materials at temperature 900 °C. The reduction tests were performed in DTA-TG apparatus in Ar–4% H_2 atmosphere starting from room temperature up to 900 °C. Fig. 2 shows the typical non-isothermal reduction curves of the starting powder materials. It has been found that the rate of reduction of the powder increase in the order NiO > mixed powder > Fe_2O_3. At early stages of reactions, both pure iron oxide and mixed powders show very low reduction extent where the low reduction temperature is still not enough to accelerate the rate of reduction. The observed lower rate of iron oxide is owing to formation of lower iron oxide like wüstite and magnetite where the reduction of iron oxides takes place in a stepwise manner. For mixed powder (50 wt% NiO), the presence of NiO with iron oxide plays a considerable role in the rate of reduction and greatly affects the morphological changes accompanying reduction process. It can be noticed that the presence of NiO increases the overall rate of reduction where NiO is reduced first then the metallic phase of Ni acts as a catalyst and promotes the reduction rate of iron oxides.

The isothermal reduction behavior of iron oxide–nickel oxide mixture was followed thermo-gravimetrically at 900–1200 °C in Ar–4% H_2 atmosphere. The extents of reduction were calculated as a function of time and the reduction curves and reduction rates were plotted as given in Fig. 3. The obtained reduction curves are reflecting the effect of temperature on the reduction rate through the whole reduction stages. For each reduction curve, the rate of reduction was highest at early stages and gradually decreased with time till the end of the experiment. It can be seen that the extent of reduction increased as the reduction temperature increased both at the initial and final reaction stages.

In order to predict the rate controlling mechanism at both the initial and final stages of reduction, the values of apparent activation energy (E_a) were calculated from Arrhenius equation:

$$K_r = K_o e^{-E_a/RT}$$

where K_r is the reduction rate constant, K_o is the frequency factor, R is the gas constant and T is the absolute temperature. The relationships between the logarithm of the rate of reduction (dr/dt) and the reciprocal of the absolute temperature $1/T$ are plotted at different reaction stages as shown in Fig. 4. From the obtained results, the apparent activation energy (E_a) values were calculated at initial and final stages of

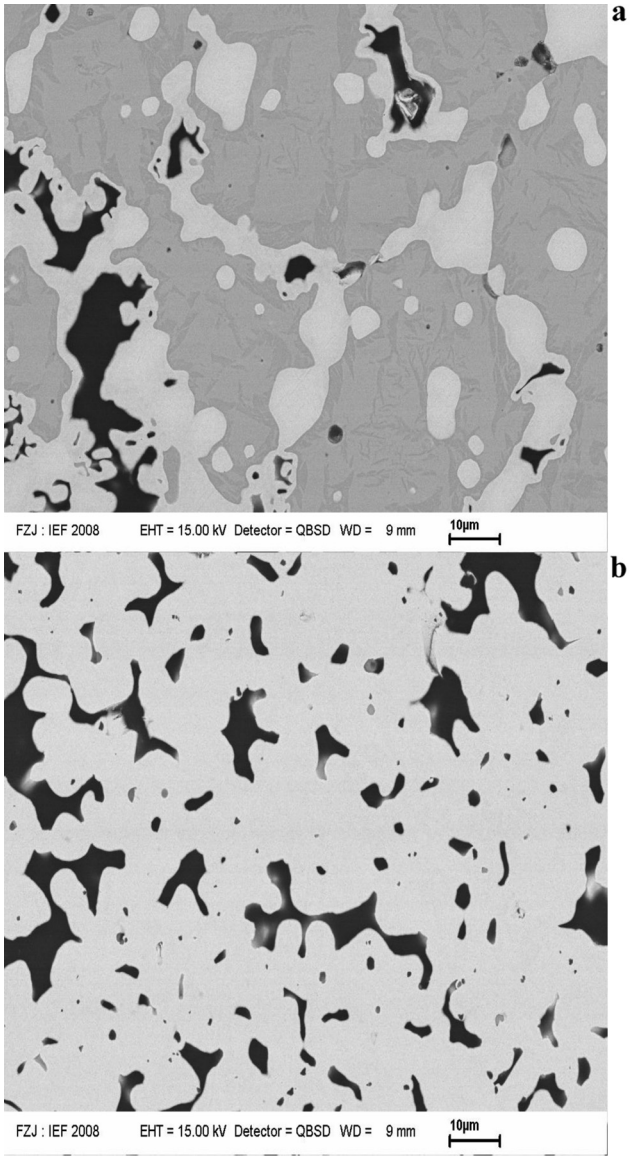

Fig. 7 – SEM images of Fe_2O_3 and NiO compacts simultaneously reduced-sintered at 1000 °C in Ar–4% H_2 gas for 10 h: (a) 10% NiO. (b) 50% NiO.

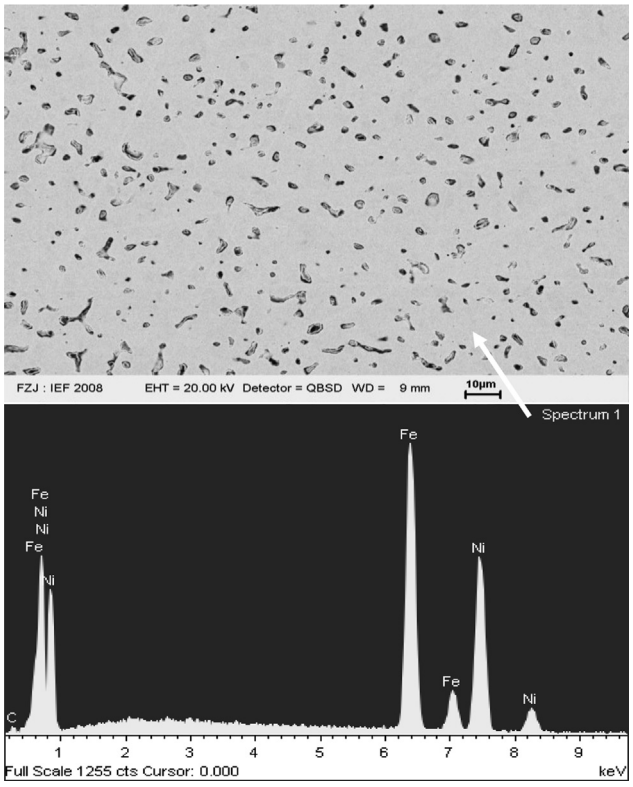

Fig. 8 – SEM image with EDX analysis of Fe_2O_3 and 50% NiO.

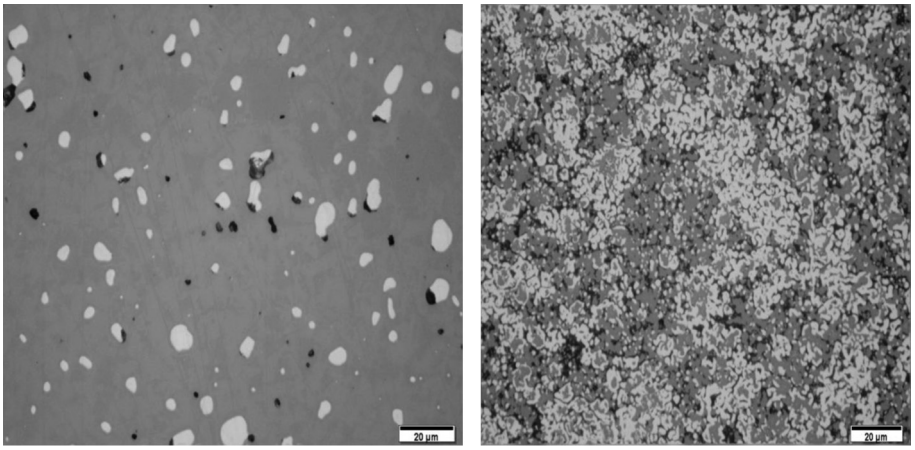

Fig. 9 – Photomicrographs of Fe_2O_3 and NiO compacts simultaneously reduced–sintered at 1000 °C in Ar–4% H_2 gas for 5 h: (a) 10% NiO. (b) 50% NiO.

reduction. The calculated activation energy values indicate that the reduction at both the initial and moderate stages (20–60% reduction extent) is most likely controlled by a combined effect of gaseous diffusion and interfacial chemical reaction mechanisms (E_a ~ 40–50 kJ/mol). At the final reduction stages (90%), the calculated values of activation energy indicate that the reduction is most likely controlled by gaseous diffusion mechanism (E_a ~ 26 kJ/mol). The variation of activation energy values can be attributed to the microstructural changes accompanying the reduction reactions.

3.2. *Sintering–reduction technique for fabrication of ferroalloys*

The produced metallic materials (Fe, Ni) alloy is characterized by unique physical and mechanical properties. The reduced products were characterized with X-ray diffraction analysis as shown in Fig. 5. It was found that the iron–nickel alloy was formed as $Fe_{0.64}Ni_{0.36}$ phase which is known previously from literature that such kind of alloys have faced centered cube (FCC) crystalline structure. They also are characterized by a soft magnetic nature with ferromagnetic state where the most stable state is the Fe_xNi_{1-x} ferromagnetic state at $x = 0.7$ and 0.6 (Wu et al., 2005; Jartych et al., 1999). Under the effect of heat treatment in reducing atmosphere both iron oxide and nickel oxide were decomposed and reduced to lower oxides and further to Ni and Fe metal. These metallic particles formed Fe–Ni alloy in FCC crystalline structure ($Fe_{0.64}Ni_{0.36}$). The results of X-ray measurements were confirmed using instrumental chemical analysis (ICP analysis) as shown in Table 2, from which it can be concluded that metallic Fe and Ni only exist after reduction experiment.

The main advantage of produced metallic alloys is their narrow particle size distribution leading to a well-defined pore size distribution during sintering and reduction. The composition of the produced ferroalloy is greatly affected the porosity and pore size distribution (Fig. 6, Table 2).

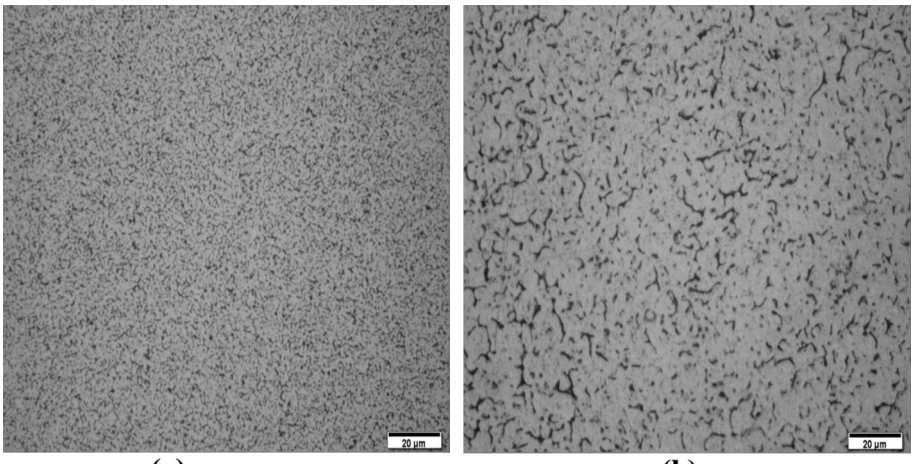

Fig. 10 – Photomicrographs of Fe_2O_3 and NiO samples simultaneously reduced–sintered at 800 °C in pure H_2 gas for 1 h: (a) 25% NiO. (b) 50% NiO.

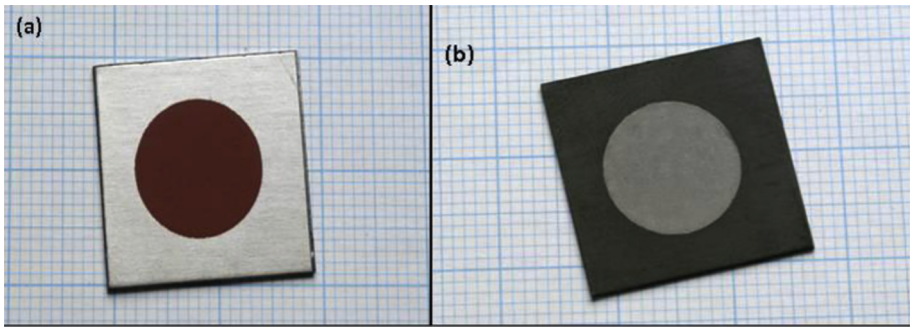

Fig. 11 – Photographs of the screen printed samples: (a) metal oxides screen printed over dense steel substrate. (b) Sample (a) after sintering–reduction reaction.

The microstructure changes accompanying sintering–reduction processes were investigated under different experimental parameters such as temperature, holding time and gas composition. Morphologically, the produced metallic structure has either less porous structure as agglomerated grains or very highly porous structure like flower-shape (Abdel Halim et al., 2006). The morphology of the produced alloy from metal oxides compacts reduced at 1000 °C in Ar/4% H_2 gas for 10 h is shown in Fig. 7. For compact with low percent of NiO (10 wt% NiO), different phases can be detected which indicate incomplete reduction extent. The gray phase could be wüstite phase which resist the further reduction reactions. Whereas for sample with high content of NiO (50 wt% NiO), a relatively less porous structure composed mainly of $Fe_{0.64}Ni_{0.36}$ alloy with the presence of micropores and absence of macropores. In such kind of metal oxides matrix, the presence of metallic Ni enhances the reduction process and accelerates the rate of reduction as it acts as a catalyst. The morphology of the produced alloy is also greatly affected by the holding time of reduction–sintering reaction as shown in Fig. 8 for samples reduced at 1000 °C in Ar/4% H_2 gas for 5 h. It can be reported that the time of the reaction is not enough for complete reduction of metal oxides even with high NiO content (Fig. 8). Different phases of metallic, wüstite, magnetite and even hematite phase can be easily observed in both matrixes with low and high contents of NiO.

The gas composition is also playing a vital role in the production of these ferroalloys. Fig. 9 shows the SEM image with EDX analysis of metal oxides (50 wt% NiO) completely reduced at 1000 °C in pure H_2 gas for 3 h. It can be observed that the produced ferroalloy is formed in a very dense structure with the presence of few micropores. Accordingly, the decrease in reduction temperature and/or holding time is necessary to optimize the porosity of the produced ferroalloy. Fig. 10 shows photomicrographs of metal oxides completely reduced in pure H_2 gas at 800 °C for 1 h. A homogenous porous structure can be observed. No gray phases of wüstite or other iron phase can be detected which means that pure ferroalloy has been formed. Based on the above morphology background, the using of ferroalloy for membrane applications could be investigated in the range of reduction temperature between 800 and 1000 °C and in pure H_2 gas for 1–3 h.

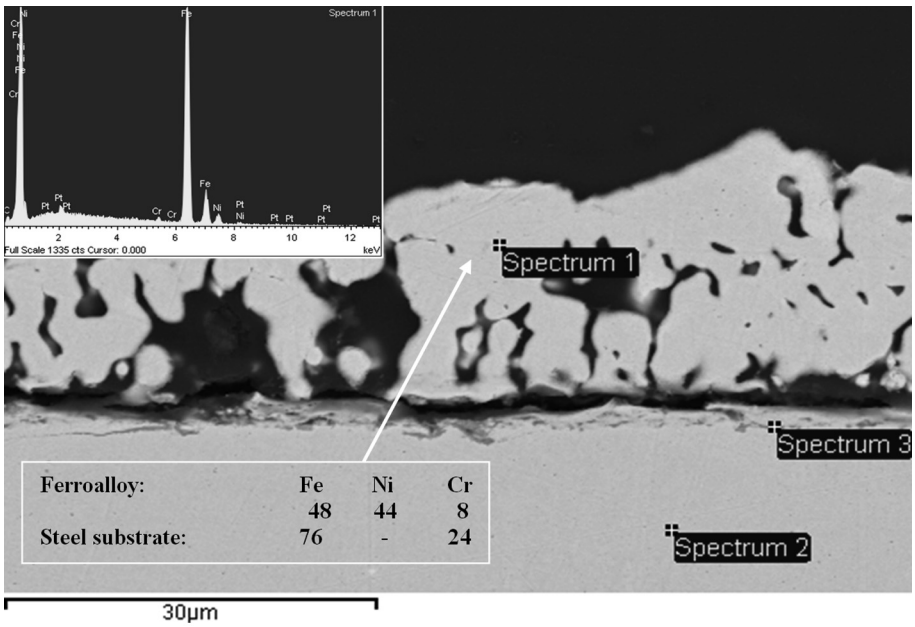

Fig. 12 – Photomicrographs of iron oxide and 50% NiO screen printed on steel substrate after reduction in H_2 at 800 °C for 3 h.

3.3. *Fe–Ni alloy for membrane applications*

The produced ferroalloy is tested for membrane fabrication. Screen printing technique was used for deposition of mixed metal oxides layer over dense crop steel substrate. The dry printed substrate was sintered–reduced under different operation parameters. Fig. 11 shows the photographs of screen printed samples before and after experiment. The observed color of the deposited layer is bright red before the experiment which represents the color of hematite and it turns gray after the experiment due to the formation of metallic layers resulting from sintering–reduction reactions.

A cross section of metal oxide screen printed on dense steel substrate and completely reduced at 800 °C for 1 h in pure H_2 is shown in Fig. 12. A porous ferroalloy layer is deposited on the substrate and its composition was confirmed by EDX analysis. The ferroalloy was found mainly composed of high content of iron and Ni. The composition of ferroalloys is often a key element to control its properties. The inter-diffusion of metallic Cr from steel substrate to the deposited layer forming ternary system ferroalloy composed of Fe, Ni and Cr is amazing phenomena in such operation conditions and assumed significant issue for the produced membrane. It was found that ferroalloy layer with relatively high content of chromium metal (8%) is deposited on the steel substrate (Fig. 12), which reflect the possibility of forming metallic membrane with two homogenous layer composed of (Fe, Cr) Ni alloy.

4. Conclusion

Inorganic metallic membrane made of ferroalloy layer deposited on steel substrate was developed for microfiltration devices via thermal route of simultaneously sintering–reduction techniques. Fabrication of porous Fe–Ni alloy has been tested by simultaneous reduction–sintering reactions of iron oxides doped nickel oxide. Screen printing technique was used for the deposition of the mixed powder of Fe_2O_3 doped NiO on the steel substrate layer.

It was found that pure $Fe_{0.64}Ni_{0.36}$ with relatively high porosity can be fabricated via reduction route. The presence of NiO increases the overall rate of reduction where NiO is reduced first then the metallic phase of Ni acts as a catalyst and promotes the reduction rate of iron oxides. The calculated activation energy values indicate that the reduction at both the initial and moderate stages is most likely controlled by a combined effect of gaseous diffusion and interfacial chemical reaction mechanisms. At the final reduction stages, the calculated values of activation energy indicate that the reduction is most likely controlled by gaseous diffusion mechanism.

The microstructure changes accompanying sintering–reduction processes were investigated under different experimental parameters such as temperature, holding time and gas composition. The obtained results were used to optimize the conditions of deposition ferroalloy layer on steel substrate. It was found that porous ferroalloy layer composed of Fe, Ni and Cr can be achieved under optimal experimental conditions.

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