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Microstructure and Properties of Gravity Sintered 316L Stainless Steel Powder with Nickel boride Addition

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Abstract:

The present work demonstrates a procedure for synthesis of stainless steel powder by gravity sintering method. As an additive to the basic powder, NiB powder was added in the amount of 0.2 - 1.0 wt.% . Gravity sintering was done in vacuum, at the temperatures of 1100 °C - 1250 °C, in the course of 3 - 60 min, using ceramic mould. Structural characterization was conducted by XRD, and microstructural analysis by optical and scanning electron microscope (SEM). Mechanical properties were investigated by tensile tests with steel rings. Density and permeability were determined by standard techniques for porous samples. Gravity sintered stainless steel with NiB addition had more superior mechanical and physico-chemical properties compared to stainless steel obtained by standard powder metallurgy procedures – pressing and sintering.

Keywords: *Stainless steel filters, Gravity sintering, NiB additive, Microstructure, Mechanical and physical properties.*

1. Introduction

Filters from stainless steel alloys are used as prefilters for all types of fluids. They are mostly used for filtration of water in water and beverage bottling plants, sparging of wine and oil (any liquid fluid that requires inert atmosphere), in petrochemical, electric power and pharmaceutical industry. These filters are more efficient in purification process due to their higher capacity for retaining impurities and higher pressure drop. They also show better properties compared to currently widely applied polymer filters limited by exposition time, compatibility and application of higher temperature and viscosity [1-4].

Compaction methods and sintering are normally required to produce filter materials from stainless steel. Porous parts from this alloy can also result from using gravity sintering process without compaction of the powder. However, differently to e.g. bronze based filters most often obtained this way, gravity sintering of stainless steel is still impractical and used only in cases requiring lower-density and higher-permeability parts [5]. The main reason for avoiding this sintering procedure is the presence of stable oxides on the surface of every stainless steel powder particle. In the conventional methods of pressing and sintering, irregularly shaped particles are used as a starting material since they are more compressible than the spherical form. For their part, spherical particles are more desirable in the production of filters because they ensure more uniform pore distribution and therefore better physical properties. However, the use of spherical particles is undesirable due to low green density of the pressed samples. In order to use the advantages provided by spherical particles and apply

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the simplest filter production technique – gravity sintering, the addition of certain additives to stainless steel powder was considered which would help optimize the densification of the starting material in the gravity sintering process. Most often used additives are B, FeB, CrB, NiB, BN, Si and Sn in small concentrations (0.15 – 5 wt.%). These additives form liquid phase with the basic material at certain temperatures, thus activating the sintering process [6-12]. It should be stressed out that the selection of additive is crucial in the process of liquid phase sintering, since its characteristics directly influence the properties of final product. In this work, NiB was the additive of choice because it reduces stable oxides from the surface of stainless steel particles and forms easily meltable eutectics with Fe and Ni from prealloyed steel powder. Also, compared to elemental boron this compound is less reactive and is characterized by better control of liquid phase formation [6].

The aim of this work was to obtain porous, filter material from stainless steel by liquid phase sintering process, with mechanical and physico-chemical properties comparable with or better than the same products synthesized by conventional powder metallurgy procedures of pressing and sintering.

2. Experimental procedure

The starting materials consisted of spherical stainless steel powder, commercial grade SURFIT TM 316L, with particles below 90 μm, and NiB powder with mean particle size of 1.2 μm. NiB powder was obtained from elemental Ni and B powders mixed in 83:17 ratio (wt.%) in Turbula mixer for 60 min. The mixture was uniaxially pressed at the pressure of 150 MPa and then the pressed samples were heated to 970 °C for 60 min in argon. Sintered NiB chips were finally milled in attritor for 480 min in argon. Homogenization of steel and additive powders, with different NiB content, 0.2; 0.4; 0.6; 0.8 and 1.0 (wt.%), was also conducted in Turbula mixer during 120 to 480 min. Homogenized mixture of stainless steel and NiB powders was sintered in vacuum at temperatures 1100 °C, 1150 °C, 1200 °C and 1250 °C, during different times: 3, 15, 30, 45 and 60 min, in high-density alumina mold designed for obtaining porous tubes. Heating speed from room to sintering temperature was 8 °C/min, while the cooling speed after retention at the sintering temperature was 20 °C/min.

Standard procedure for obtaining porous stainless steel tubes comprised uniaxial pressing in tool steel mold at the pressure of 150 MPa and sintering in vacuum at 1100 °C for 30 min. Approximate final dimensions of porous tubes were: D = 50 mm, d = 46 mm, H = 100 mm.

Structural analysis of the powders was conducted by XRD (Bruker system3 SAXS, Ultima IV type 2 with Cu Kα Ni filtered radiation), microstructure was analyzed by optical and scanning electron microscope (JEOL-JSM 5800LV), while mechanical tests were done according to standard ISO 30911-6 applying tensile tests on rings with dimensions D = 50 mm, d = 46 mm, H = 20 mm. Vickers microhardness of samples was measured under the load of 15 g using MicroMet Vickers Microindentation Hardness Tester (Buehler, model 5101) (ASTM E 384-99). Physical characteristics: density/porosity and permeability, were determined by appropriate standards for porous materials: ASTM B 962-08 and ISO 4022, respectively. Fracture surface was analyzed by scanning electron microscopy (SEM).

The amount of released Ni ions in the liquid phase was determined by leaching tests using flame atomic emission spectroscopy (AAS Analyst 700/Perkin-Elmer). Samples were immersed in 50 ml of distilled water for 30 days at room temperature.

3. Results and discussion

Generally, a number of variable parameters affect the liquid phase sintering process.

These parameters are connected to the material characteristics influencing the process, which significantly determines sintering rate and development of the microstructure. For example, solid phase can be soluble or insoluble in liquid phase; liquid may or may not wet the solid phase, or penetrate through solid-solid grain boundaries. These phenomena, connected to particle size of the base material and additive, temperature and time of sintering, atmosphere in which the process is conducted, have a great impact on the quality of material obtained by liquid phase sintering [13]. As the aim of this work was to obtain porous samples with good mechanical and filtering properties, variable parameters of the liquid phase sintering process which were of particular interest to us were particle characteristics of the base alloy, additive and the mixture of these two powders, as well as the sintering temperature and time.

Stainless steel powder was obtained by gas atomization. It is predominantly spherical, with certain number of particles retaining satellites formed during cooling of droplets in the process of atomization. In the course of liquid jet disintegration by argon, smaller droplets solidified more rapidly and came into contact with partly solidified larger droplets (Fig. 1). Aside from spherical particle shape, chosen to ensure more uniform pore distribution in sintered samples, relatively small fraction of stainless steel powder was used in this work with over 90 % of particles between 63 and 90 μm. Smaller particles were not at our disposal, while we did not use larger particles (over 90 μm) in order to lower the size segregation in the process of mixing with NiB powder, and also to avoid abnormal grain growth and large pores in the structure of sintered product.

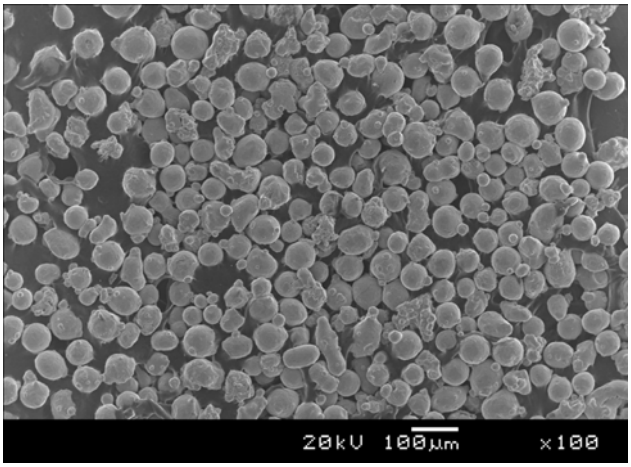

Fig. 1. 316L stainless steel powder with particle size below 90 μm.

Main reasons why NiB compound was chosen as an additive were already mentioned in the Introduction part. X-ray analysis of NiB powder showed that it consisted of particles of different nickel-boride compounds, i.e. elemental particles of the starting Ni and B powders were not identified (Fig. 2).

It is known that the addition of additive for intensifying densification of the base material in the process of liquid phase sintering can be done in several ways: manufacturing of prealloyed powder of the base material with additive [14, 15], coating of the base material particles with additive particles [6], mixing of the base material and additive powders [16]. In this work latter method was used which is, compared to other two, simpler and more economical, while its level of successfulness was controlled through NiB particle distribution in the powder mixture. This was an important phase in our experimental work due to direct influence of the mixture homogeneity on the speed and degree of powder densification in the process of liquid phase sintering. Better distribution of NiB particles in the mixture enables better packaging of its particles, promotes stages of rearranging and rapid initial densification during liquid phase sintering, as well as more homogeneous contraction of the samples during

process. The main parameters influencing the efficiency of mixing two or three different powders are: fullness of the mixing container, rotating speed of the container and time of mixing [17]. Optimum values of these parameters are mostly kept secret by the manufacturer or are patent protected. In other words, for every combination of powders (shape and size of the mixture powder particles, additive content) and mixing containers, it is necessary to experimentally determine best mixing conditions. In our work, from these three mixing parameters, we took as the only variable mixing time which was 120, 240, 360 and 480 minutes (Fig. 3). In cylindrically shaped mixers such as the one used here, optimum powder content is in the interval from 20 to 40 vol.% of the container volume [18]. We kept this parameter constant and in every experiment powder mixture content was 30 vol.% of the cylinder volume. Mixture speed was also constant and equal to 250 rounds per minute.

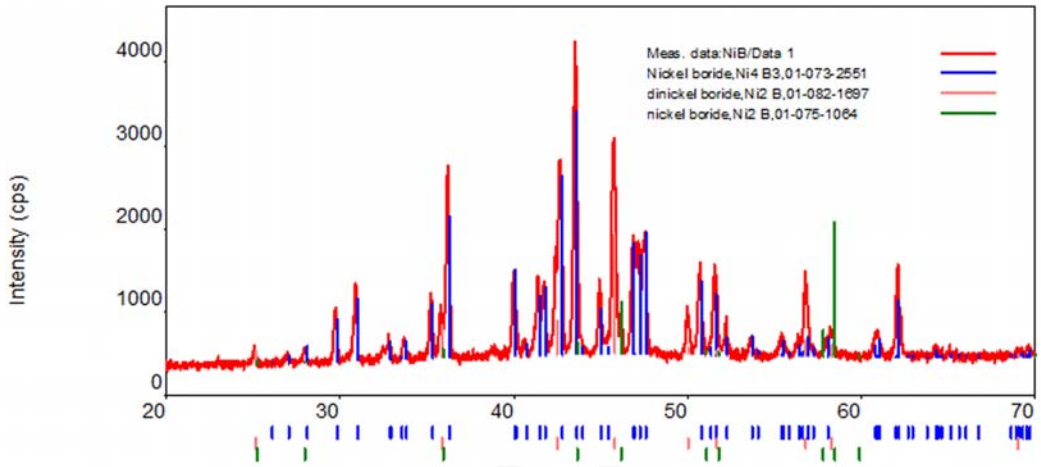

Fig. 2. Diffractogram of the NiB powder.

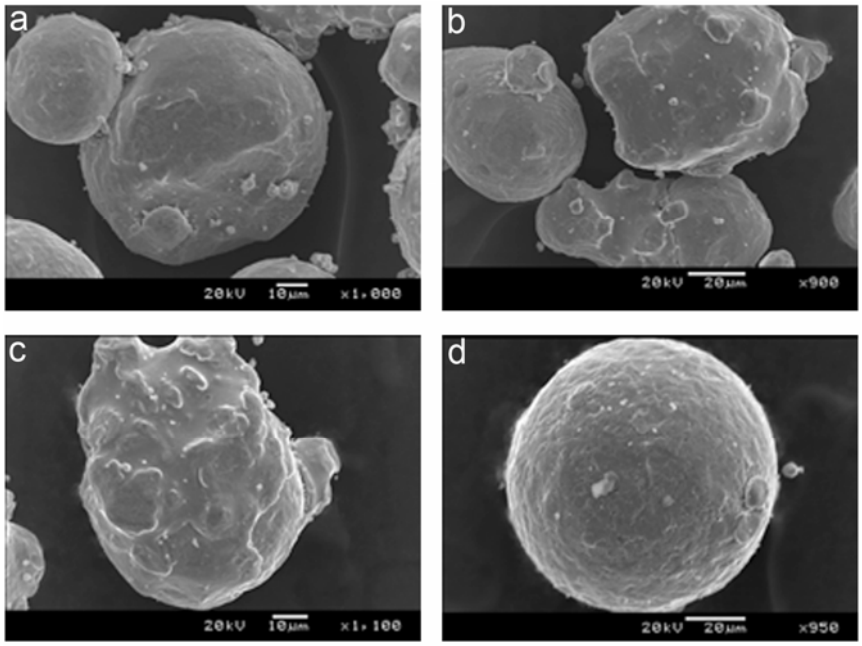

Fig. 3. SEM. Distribution of NiB powder particles on the surface of stainless steel particles. Mixing time: a) 120 min, b) 240 min, c) 360 min, d) 480 min.

Fig. 3 clearly shows the presence of agglomerated NiB particles on the surface of base powder, as well as areas without additive after 120 minutes of treating in mixer. This

time was too short to enable breaking of the bonds between submicron additives particles established in the process of their obtaining, which directly reflected on worse NiB powder particles distribution on the surface of steel particles (Fig. 3a). After 240 minutes of mixing (Fig. 3b) there is a partial breakage of these electrostatic forces between the smallest additive particles, which improved their distribution on the steel surface, reaching its optimum only after 360 minutes (Fig. 3c). Prolonged mixing time leads to over mixing of powders [17] and lowered mixture homogeneity (Fig. 3d).

Additive content in the liquid phase sintering process is, generally, different depending on which additive is used and what should be the final properties of the sintered product. Predominantly, NiB concentration added to stainless steel powder is in the interval from 0.2 to 1.0 wt.% [6, 16]. Fig. 4a depicts the influence of NiB content on the density of samples sintered at 1150 °C, 30 min. Addition of less than 0.2 wt.% NiB did not affect densification much since the amount of eutectic liquid at this temperature was insufficient to cause densification. Character of the curve in Fig. 4a is logical and expected. Higher additive content enabled formation of larger amount of liquid which directly reflected on the densification kinetics, i.e. increasing of the sintered density. An interesting fact, and in agreement with the results of other authors [16], is that NiB contents of 0.8 and 1.0 wt.% had almost the same effect on the sintered density in porous sample. In further work we used the lower concentration (0.8 wt.%) having in mind that every increase in liquid phase content degrades physical properties of filters [6].

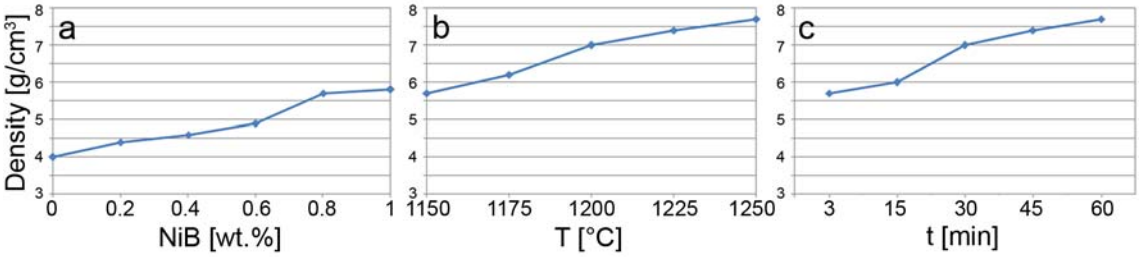

Fig. 4. Effect of NiB addition, sintering temperature and time on the sintered density: a) NiB addition, b) sintering temperature, c) sintering time.

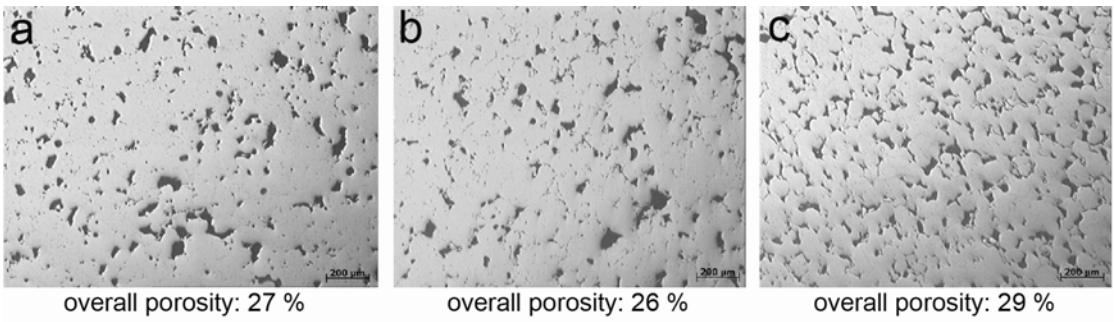

Fig. 5. OM. Microstructure of 316L-0.8wt.%NiB sintered samples: a) T = 1250 °C, t = 3 min, b) T = 1150 °C, t = 60 min, c) T = 1150 °C, t = 30 min.

It can be seen from Fig. 4 that increased temperature and prolonged time of sintering have the same effect on densification degree of the mixture as increased NiB content. The presence of NiB particles enabled around 1150 °C formation of liquid phase, i.e. low-melting eutectic formed by Fe and B [6, 16, 19]. Boron-rich liquid phase has very low solubility in iron [9] and remains as an almost continuous network between solid grains. This formed liquid improves mass transport phenomena, promotes rearrangement and fragmentation of particles. These processes become more and more intense with increased additive content, higher temperature and prolonged sintering time. As mentioned earlier, the goal of this work

is to obtain filters with good mechanical and physical properties using liquid phase sintering, which meant to direct further investigations towards samples with overall porosity of around 30 %. Fig. 5a-c represents microstructures of the samples sintered under different conditions with approximate density values, i.e. overall porosity of ~30 %.

It can be noted that short process times, due to phenomena present in the initial stadium of sintering (particle rearrangement, occurrence of liquid phase, action of capillary forces), result in less homogeneous structure (Fig. 5a), while somewhat longer sintering times cause in certain locations "extrusion" of liquid from areas around steel particles, leading to less favorable pore distribution in the sample (Fig. 5b). In our case, the best pore arrangement was obtained for sintering at 1150 °C, 30 min (Fig. 5c).

Typical microstructure obtained for stainless steel with addition of NiB consists of austenite matrix and eutectic constituent at the grain boundaries, Fig. 6. In order to distinguish the difference in chemical composition in eutectic constituent and matrix after sintering, a detailed EDS analysis was performed.

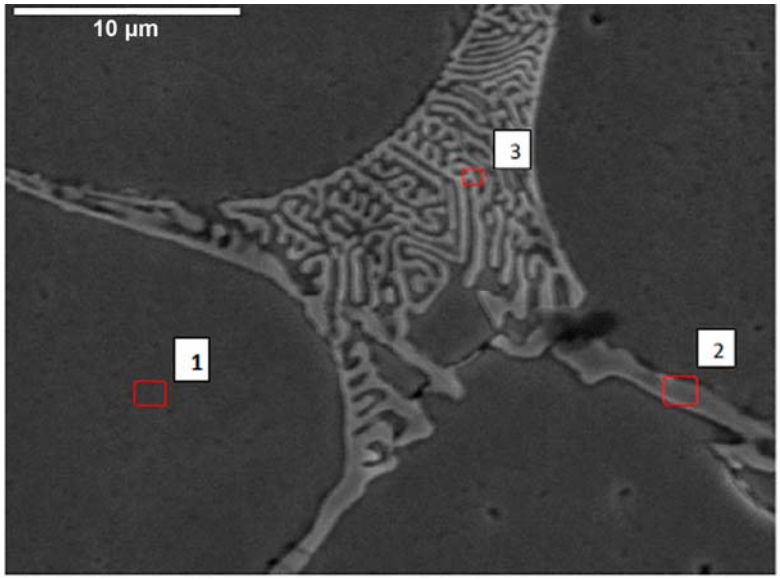

Fig. 6. SEM. Microstructure of the matrix and formed eutectic 316L-0.8wt.% NiB sample sintered at 1150 ^{o}C, 30 min.

Inserted EDS spectrum shows the presence of elements in matrix and eutectic. Compared to matrix, elemental composition is different in formed eutectic (Tab. I). For our sintering conditions (1150 °C, 30 min), eutectic was composed of chrome-rich borides (locations 2 and 3) and, to a lesser extent, molybdenum-rich borides (location 3) which precipitate more intensively only at temperatures over 1200 °C [19]. Content of other elements present in eutectic (Fe, Ni, Si) was lower compared to matrix.

Tab. I Results of EDS measurements.

1-Matrix (wt.%)	2-Cr-rich precipitation (wt.%)	3-Cr (Mo)-rich precipitation (wt.%)
Si – 1.0	Si- 0.41	Si- 0.44
Cr- 16.58	Cr- 36.07	Cr-25.27
Fe- 64.92	Fe- 50.21	Fe- 54.00
Ni- 14.50	Ni- 8.70	Ni- 9.71
Mo- 3.0	Mo- 4.61	Mo- 10.58

These precipitates, i.e. borides formed between particles of base material, had a direct effect on mechanical and physical properties of gravity sintered samples, which could be

observed from the comparison with the values of alloy having the same overall porosity but obtained by conventional processes of pressing and sintering, Tab. II.

Tab. II Values of physico-chemical and mechanical properties of sintered stainless steels obtained by different techniques.

Condition	Overall porosity, %	Open porosity, %	Permeability coefficients, α, 10^{-12} m^2/ β, 10^{-7} m	Ni content in distilled water, mg/L[1]	Ring tensile strength, MPa	Microhardness[2], $HV_{0.025}$
Pressing and sintering 316L	30	26	1.09/0.25	0.51	110	113
Gravity sintering 316L-0.8wt.%NiB	30	29	3.66/1.69	0.06	150	145

[1] Samples kept 21 day in distilled water (empty probe: 0.01 mg/L).
[2] Microhardness measured in particle contacts area.

Tab. II shows that the values of hardness are more superior in gravity sintered steel. Direct cause of better properties originates from the nature of necks formed between steel particles. In gravity sintered steel, borides in the contact areas (Fig. 7a-c), enriched first of all with chromium, are carriers of strength and ductility. It can be observed from these figures that in certain locations formed contact necks stayed compact, i.e. they withstood the action of outer force. In pressed and sintered steel, contact areas (Fig. 7d-e) contained only the elements of matrix material and formed necks featured worse mechanical properties, therefore fractures in these locations occurred more easily. The results of microhardness measurements in the areas of particle contacts exhibited trend similar to that of ring tensile strength.

It can be stated based on Tab. II that the values of permeability coefficient for air were better in gravity sintered steel compared to pressed and sintered sample of the same density. The presence of spherical particles and more uniform distribution of pores in the structure, as well as somewhat higher percent of open porosity were the reasons for obtaining more superior value of this filter property in gravity sintered steel. Another important characteristic, concentration of Ni in water, was determined for both samples (Tab. II). Namely, carcinogenic property of nickel is known, so due to passive leaking of Ni ions from the surface of stainless steel [20], concentration of this element was established for samples after three weeks of keeping them in distilled water. The obtained value of Ni concentration in water in gravity sintered steel is nearly one order lower than the concentration of this element in the water where pressed and sintered sample was held. More intensive Ni ion leakage from the surface of gravity sintered sample was prevented by the formation of precipitates which, apart from chromium borides and in lesser extent molybdenum borides, contained Ni and Fe (Tab. I).

The results obtained in this work suggest that the filters from stainless steel could be successfully obtained by sintering without previous force action of the starting powder, appropriate additive, as well as basic parameters of powder mixing and sintering process would be chosen correctly.

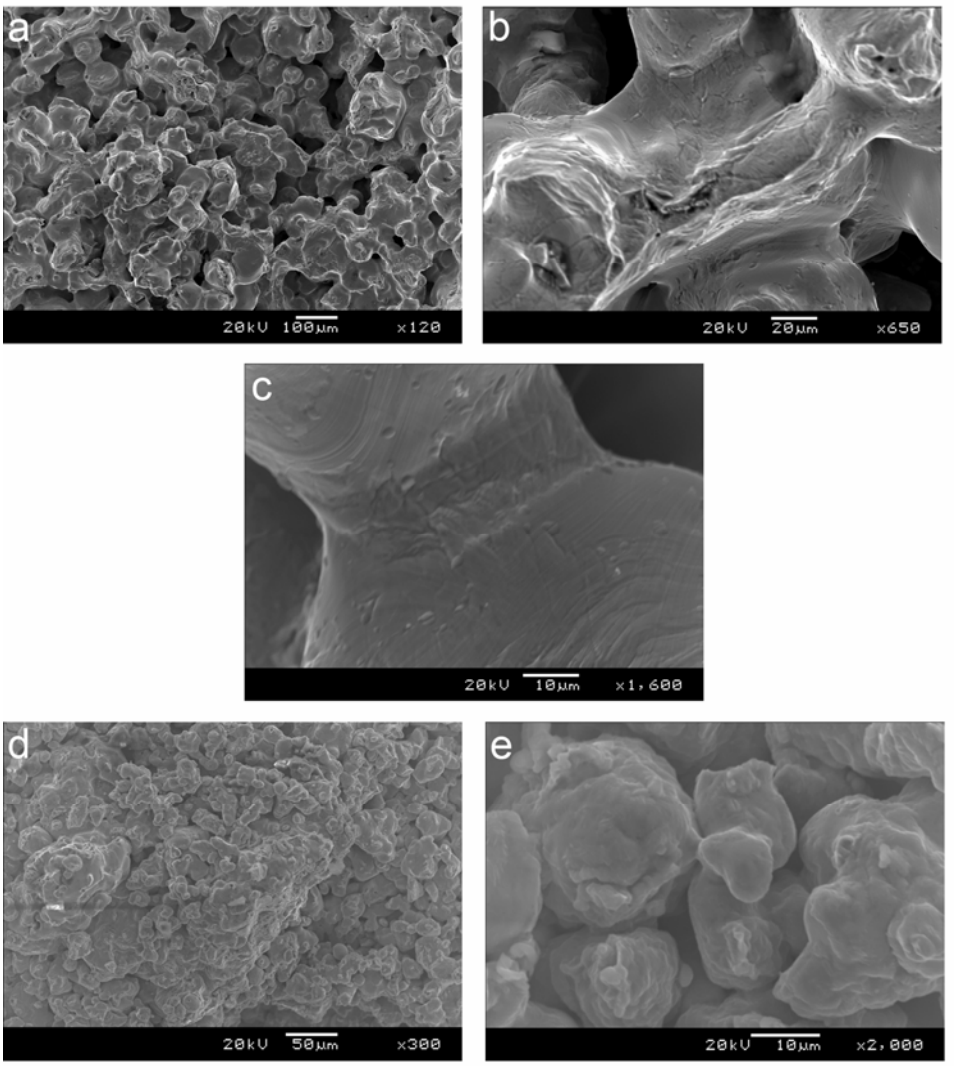

Fig. 7. SEM. Fractographs of the samples obtained by different techniques: a-c) gravity sintering of 316L-0.8wt.% NiB at 1150 °C, 30 min, d-e) pressing and sintering of 316L at 1100 °C, 30 min.

4. Conclusions

Sintering of loose 316L stainless steel powders to produce filter materials was attempted using NiB sintering activators. Experimental results showed that the mixing time of starting powders is important parameter in obtaining homogeneous mixture and that the liquid phase appeared during sintering at 1150 °C, for 30 min. Borides were formed and eutectic reactions between borides and 316L stainless steel occurred during sintering. Liquid phase stays as a nearly continuous network between solid grains. The density of gravity sintered samples increases with increasing boron content, and also with increased temperature and prolonged time of sintering. In gravity sintered steel 316 L-0.8 wt.% NiB obtained by sintering at 1150 °C for 30 min, aside from Fe and Ni eutectic had significant content of Cr-rich borides and a lot less Mo-rich borides. Mechanical and physico-chemical properties were more superior compared to properties obtained in pressed and sintered 316L steel of the same overall porosity.

Acknowledgements

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Садржај: *Представљен рад даје поступак синтезе праха од нерђајућег челика коришћењем методе гравитационог синтеровања. Полазни материјал се састојао од мешавине прахова нерђајућег челика и NiB, при чему је садржај NiB честица износио 0.2-1.0 теж.%. Гравитационо синтеровање је извршено у вакууму, на температурама од 1100 °C - 1250 °C, при временима задржавања од 3 - 60 min, коришћењем керамичког калупа. Структурна карактеризација извршена је помоћу XRD, а*

микроструктурна анализа коришћењем оптичког и сканирајућег електронског микроскопа (СЕМ). Механичка својства су испитивана помоћу методе затезања челичног прстена. Густина и пермеабилност су одређени стандардним техникама за порозне узорке. Гравитационо синтерован нерђајући челик са додатком NiB имао је супериорнија механичка и физичко-хемијска својства у односу на нерђајући челик добијен стандардним техникама металургије праха - пресовањем и синтеровањем.
Кључне речи: *филтери од нерђајућег челика, гравитационо синтеровање, NiB додатак, микроструктура, механичка и физичка својства*