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Properties of duplex stainless steels made by powder metallurgy

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ABSTRACT

Purpose: of this paper was to examine the mechanical properties of duplex stainless steels.

Design/methodology/approach: In presented study duplex stainless steels were obtained through powder metallurgy starting from austenitic, martensitic base powders by controlled addition of alloying elements, such as Cr, Ni, Mo and Cu. In the studies behind the preparation of mixes, Schaeffler's diagram was taken into consideration. Prepared mixes have been sintered in a vacuum furnace with argon backfilling at 1260°C for 1 h. After sintering: rapid cooling have been applied in argon atmosphere. Produced duplex stainless steels have been studied by scanning and optical microscopy. Mechanical properties such as tensile strength, impact energy, hardness and wear rate were evaluated.

Findings: According to achieved results, it was affirmed that applied sintering method as well as powder mixes preparation allows for manufacturing the sintered duplex steels with good mechanical properties which depends on austenite/ferrite ratio in the microstructure and elements partitioning between phases. The additions of alloying elements powders (promoting formation ferritic and austenitic phase) to master alloy powder, makes possible the formation of structure and properties of sintered duplex stainless steels. Sintered duplex steels obtained starting from austenitic and ferritic powders with admixture of elemental powders achieve lower mechanical properties when compared to composition obtained by mixing ferritic and austenitic powder in equal amounts.

Research limitations/implications: According to the powders characteristic, the applied fast cooling rate seems to be a good compromise for mechanical properties and microstructures, nevertheless further tests should be carried out in order to examine different cooling rates.

Originality/value: The use of elemental powders added to a stainless steel base showed its potentialities, in terms of fair compressibility and final sintered density. In addition a good microstructural homogeneity and first of all mechanical properties and corrosion resistance was achieved, also working with cycles possible for industries.

Keywords: Mechanical properties; Powder metallurgy; Duplex stainless steel; Strength

PROPERTIES

1. Introduction

Duplex stainless steels are the newest in the stainless steels family. They are characterized by a two-phase structure consisting of approximately equal amounts of ferrite and austenite. Ferritic phase is responsible of the strength increase while austenite ensures the toughness and better corrosion resistance. Duplex stainless steels thus combine some of the features of the two major classes, austenitic and ferritic grades. Such combination of properties makes the duplex stainless steels very attractive for numerous applications.

Sintered stainless steels are used in many industrial branches due to their high mechanical properties and good corrosion resistance. According to profitability, high dimensional tolerance, shape reproducibility and energy saving the main receiver of parts produced by powder technology is automotive appliances industries. The powder metallurgy stainless steels, especially ferritic grades, have found applications in mounting brackets for the rear view mirrors, the tone wheels for the antilock brake systems and also in automotive exhaust applications like exhaust flanges and mounting unit of HEGOS. The automotive market introduces newly designed sintered parts in large amounts in produced cars. The new cars constructions are equipped with at least six powder metal flanges piece. Stainless steel is the preferred material for powder metal flanges because of its resistance to corrosion and oxidation. The fact that the powder metal parts can be made in high material densities for the optimum combination of properties has encouraged their use at Ford and at General Motors Corp.- the two biggest users of powder metal exhaust system flanges in the world. The usage of automobile parts manufactured by powder metallurgy in still weak in Europe and Japan (Fig. 1), which is the reason of advanced researches on the sintered stainless steels especially easy to manufacture, cost effective and environmental friendly grades. Sintered duplex stainless steel seems to be very promising in those appliances what explain performed research in Europe [1-15].

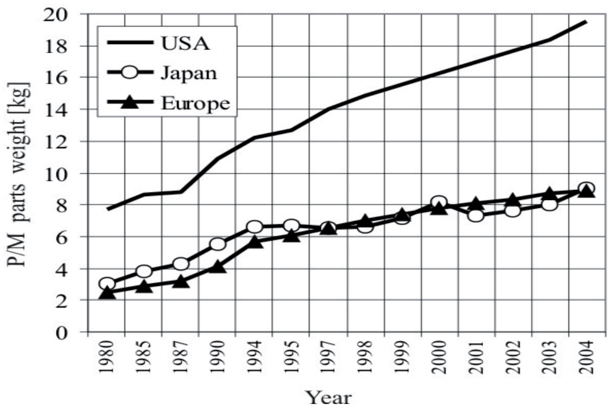

Fig. 1. Parts weight in typical vehicle made by powder metallurgy

2. Experimental procedure

Different compositions have been tested, using austenitic X2CrNiMo 17-12-2 and ferritic X6Cr13 (Fig.2) as starting base watcher atomized powders with the characteristics presented in Table 1.

Austenitic base powder X2CrNiMo 17-12-2 were mixed with addition of alloying elements powders such as Cr (in form of ferrochromium powder), Ni, Mo and Cu in the right quantity to obtain the chemical composition similar to biphasic one - mixtures A and B. Powder mixtures signed as C and D were produced starting from ferritic powder X6Cr13. Moreover, the ferritic stainless steel X6Cr17 powder has been mixed to austenitic stainless steel powder in the ratio of 1/1 in order to examine the structure derived after sintering (mixture E). In the preparation of powder mixtures, Schaffler's diagram was taken into consideration (Fig. 3).

Table 1.
Average composition of starting powders

Grade powder		Elements concentration, wt. %						
PN-EN	AISI	Ni	Cr	Si	Mn	Mo	C	Fe
X2CrNiMo 17-12-2	316L	13	17	0.8	0.2	2.2	0.02	bal.
X6Cr13	410L	0.14	12.2	0.88	0.09	-	0.02	bal.
X6Cr17	430L	-	16	1.14	0.19	-	0.09	bal.

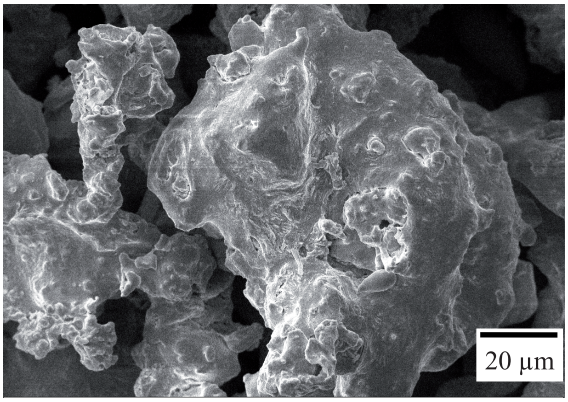

Fig. 2. X6Cr13 stainless steel powder

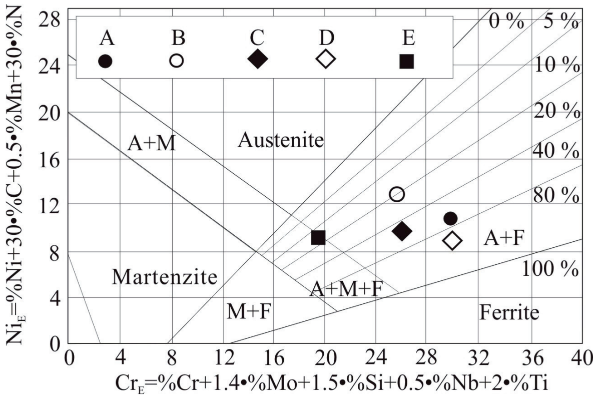

Fig. 3. Schaffler's diagram. The marked points on the graph determine the forecast structure of the compositions

Although its proper application is in welding, it is possible to extend its use in the field of powder metallurgy. Thus Cr_E and Ni_E equivalents were obtained using formulas 1 and 2 respectively.

$$Cr_E = \%Cr + \%Mo + 1.5 \cdot \%Si + 0.5 \cdot \%Nb \tag{1}$$

$$Ni_E = \%Ni + 30 \cdot \%C + 0.5 \cdot \%Mn \tag{2}$$

The weight quantities of the corresponding elements in percent were introduced in those formulas which locate all prepared powder mixtures in a well defined area, at least from a theoretical point of view. Chemical composition of produced mixtures were placed in austenitic-ferritic area of the Schaffler's diagram with various content of ferritic phase in the range from 20 to 80%.

Powders were mixed with single elements using a laboratory turbula mixer. Acrawax was used as lubricant in a quantity of 0.65 wt.% in excess 100 for all compositions produced. Samples were obtained using a hydraulic press applying a pressure of 800 MPa with a floating die. The debinding process was done at 1022°F for 60 minutes in a nitrogen atmosphere. Samples were then sintered in a vacuum furnace with argon backfilling at 2300°F for 1 h. After sintering two different cooling cycles were applied: rapid cooling with an average cooling rate of 473°F/min using nitrogen under pressure 0.6MPa and slow cooling with furnace with an average cooling rate of 41 °F/min in argon atmosphere Table 2 presents all the prepared compositions.

Table 2.
Chemical composition of investigated powder mixes

Base powders	Composition designation	Elements concentration, wt. %						
PN-EN		Ni	Cr	Si	Cu	Mn	Mo	Fe
X2CrNiMo 17-12-2	A	10.52	26.40	0.80	0.80	-	2.02	bal.
	B	11.51	21.33	0.84	2.00	-	2.21	bal.
X6Cr13	C	8.10	22.72	0.70	-	0.06	2.00	bal.
	D	8.09	26.23	0.65	2.00	0.06	2.00	bal.
X2CrNiMo 17-12-2, X6Cr17	E	6.50	16.20	1.02	0.05	0.10	1.25	bal.

Densities were evaluated using the water displacement method. Microstructure observations were carried out using LEICA MEF4A light microscope and scanning electron microscope equipped in EDS. Evaluations of the phase composition were made using ARL X'TRA 48 X-ray spectrometer, with the filtered copper lamp rays with 45kV voltage and heater current of 40mA. Metallographic specimens of all test materials were analyzed in the unetched as well as etched conditions. Unetched metallographic samples were utilized to evaluate stereological parameters of the pore structure such as pore size and pore shape factors f_s and f_e according to formula 3 and 4. This was accomplished with a Leica Qwin image analysis system. Pore shape factor f_s determine profile irregularity of a pore while pore shape factor f_e represent the pore elongation.

$$f_s = \frac{4 \cdot \pi \cdot A}{P^2} \tag{3}$$

where A and P are the area and the perimeter, respectively, of the metallographic cross-section of the pore.

$$f_e = \frac{D_{\min}}{D_{\max}} \tag{4}$$

where, Dmin and Dmax are the minimum and the maximum Feret diameter of a pore. The shape factor of 1 represents a circular pore in the plane of analysis and as the number decreases from 1, the elongation and degree of irregularity increases.

Hardness test was carried out in order to determine HRA value. Charpy impact test were made according to PN-EN 10045-1 standard on unnotched samples and tensile test according to PN-EN 10002-1 standard on samples prepared according to ISO 3928 standard.

3. Results and discusion

Sintered duplex powders were subject of studies at different universities as well as in the major companies producing powders. Application of powder metallurgy for producing ferritic-austenitic steels enables precise control of their chemical and phase composition of structure as well as elimination of numerous technological difficulties present during production of same kind of steels but using traditional methods. In order to reduce production costs of parts made from sintered duplex stainless steels, the heat treatment, so called „sinter-hardening" has been introduced, which relies on rapid convection cooling directly from sintering temperature using backfilling gas under pressure e.g. nitrogen. Application of this heat treatment method, in case of duplex stainless steels provides to obtain precipitate free structure. In the presented study density results, where evaluated using the water displacement method obtained in terms of green and sintered density (Tab. 3) and shows that for the ferritic based mixtures sintered densities were included in the range of 7.13 to 7.25 g/cm^3. For the austenitic based powders, lower values were obtained, even though starting with green values similar to the other compositions. It is remarkable to notice that, in case of mixture (B), an approximate dimensional stability was obtained. For this composition green and sintered density is in convergence. Mixture (E) obtained by mixing ferritic and austenitic powders in equal amounts shows good density after sintering cycle (Fig. 4).

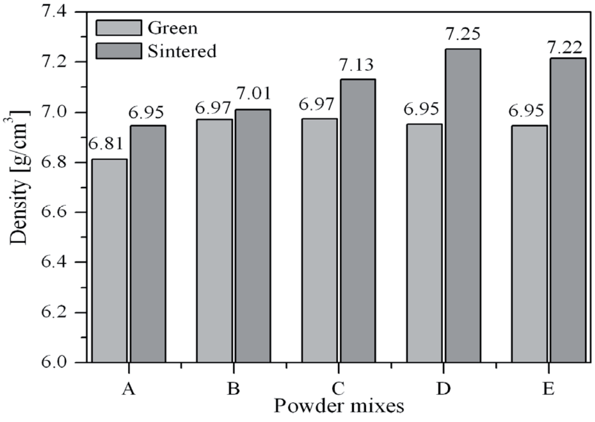

Fig. 4. Green and sintered density of studied compositions

Greater reactivity of ferritic grade powders when compared to austenitic grades results in higher shrinkage rate of the first one. The smallest shrinkage 0.5% was obtained for mixture (B) while the highest 4.1% for mixture (D) based on ferritic powder.

Moreover, the addition of copper has resulted in the formation of a liquid phase during sintering and there through it influences on growth of sinterability caused by faster mass transport. This is evident for compositions containing copper with reason of higher sintered density when compared with sintered duplex stainless steels without copper addition.

Table 3.
The results of green density, sintered density, total porosity and average pore size of studied compositions

Composition designation	Theoretical density [g/cm^3]	Green density [g/cm^3]	Sintered density [g/cm^3]	Total porosity [g/cm^3]	Shrinkage [%]	Average pore area [μm^2]
A	7.80	6.81	6.95	10.95	2.0	28.69
B	7.86	6.97	7.01	10.86	0.5	20.78
C	7.80	6.97	7.13	8.59	2.2	27.81
D	7.80	6.95	7.25	7.06	4.1	30.66
E	7.79	6.95	7.22	7.34	3.7	14.65

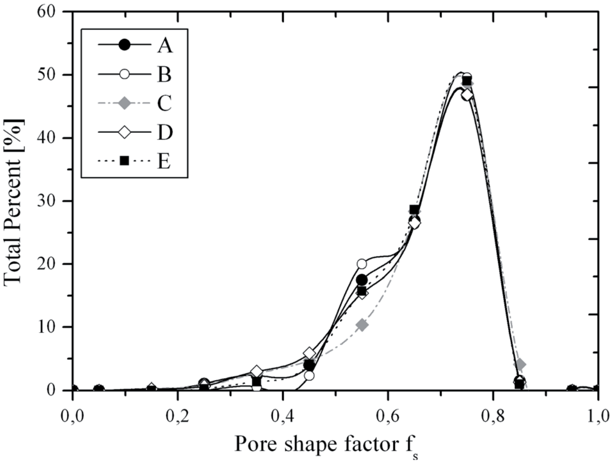

Fig. 5. Pore shape factor f_s of steels sintered and fast cooled directly from sintering temperature

Plot of pore shape factor fs indicate that for all prepared mixtures his value is much the same and the major part of pores (about 50%) achieve approximately 0.75 in the case of sintering cycle with fast cooling from sintering temperature (Fig. 5). Pore shape factor f_e demonstrate major variety of pores shape and is including in the range of 0.45-0.7. There appears to be no significant change in the pore shape for all the materials that were evaluated.

Evaluation of pore morphology in the case of sintering cycle with slow cooling after sintering indicate that pore become more spherical due to elongated temperature affect (Fig. 6). This effect is more evident for composition (E).

Performed X-ray analyses confirm that the structure of the obtained sintered steels consists of austenite and ferrite phases in the case of fast cooling directly from sintering temperature. Performed analyses do not demonstrate other secondary phases like sigma phase, carbides or nitrides precipitations in the microstructure of those steels.

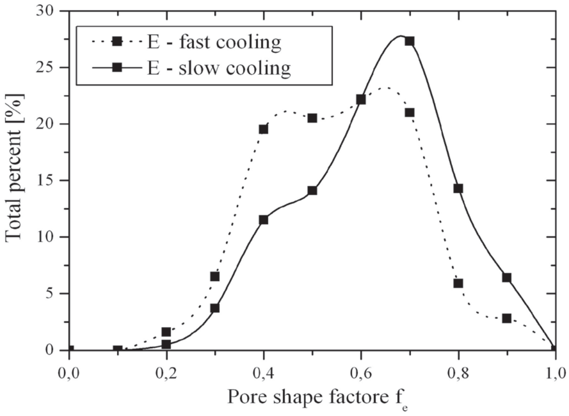

Fig. 6. Pore shape factor f_e of composition (E) cooled after sintering with different ratios

Phase quantities in the microstructure were evaluated. Composition (A) and (D) reaches the ferrite content about 75% while composition (B) 18%. For composition (C) the approximate balance of ferrite and austenite was archived. Steel marked as (E) reach ferrite content about 67%. The obtained results prove the usefulness of the Schaffler's diagram for predicting the types of sintered duplex steels structures. Figure 7 shows X-ray diffraction patterns of investigated sintered duplex steels with major diffractions from ferrite and austenite. According to metallographic examinations of obtained materials the presence of a fine microstructure with no recollection of precipitates can be seen. The microstructure of produced duplex steels is presented in Figure 8. The absence of precipitates shows that applied technology and the way of achieving mixtures result in the right microstructure. Austenite and ferrite are well mixed with an observed balancing between the two structures present throughout the sample.

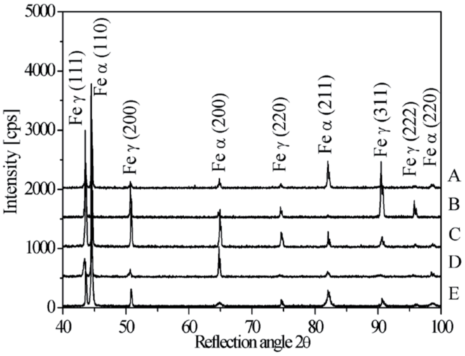

Fig. 7. X-ray diffraction patterns of sintered duplex steels

Chemical composition analysis (EDS) of individual structural components in studied steels shows (Fig. 8) that the concentrations of elements such as Cr and Mo in ferrite phase is higher, while Ni concentration is lower than in austenitic phase.

The element partitioning between ferritic and austenitic phase is consistent with the stabilizing effect of each element on the respective phase. Concentration of alloying elements in both phases is in accordance to those obtained for conventional duplex steels and additionally proves that chemical composition of structure of manufactured sintered steel corresponds to two-phase microstructure.

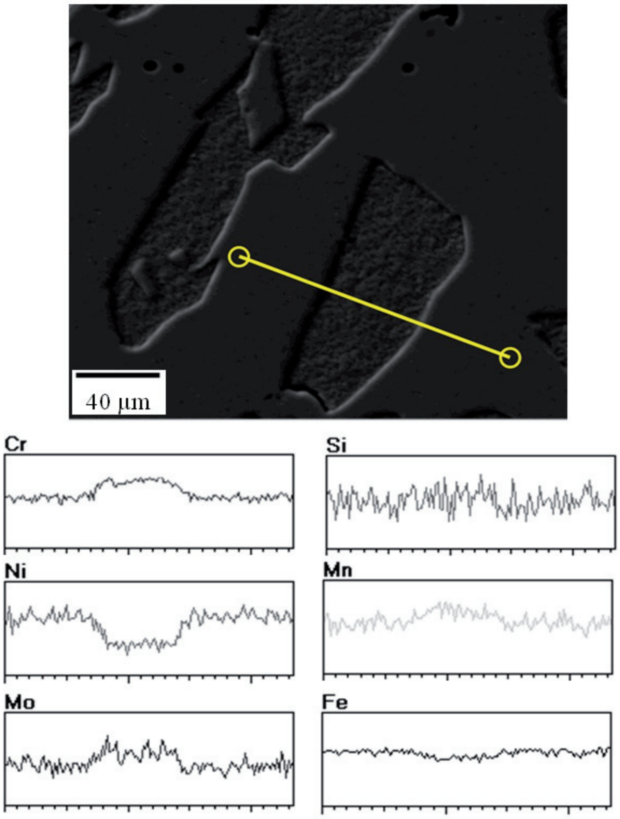

Fig. 8. Microstructure and linear distribution of alloying elements performed by EDS analysis of defined ferritic grain and surrounding austenitic region in the steel (D) obtained in sintering cycle with fast cooling rate

In the case of sintered cycle with slow cooling with furnace, precipitation on sigma phase can be seen (Figs 9, 10), except composition (E). Intermetallic sigma phase, rich in Cr and Mo precipitate on ferrite-austenite boundaries and inside ferritic grains. During cooling with slow rate, ferrites decompose on sigma phase and secondary austenite according to transformation: (ferrite → sigma + austenite) causing impoverishment of surrounded zones in alloying elements.

Mechanical properties of sintered duplex steels fast cooled after sintering cycle achieve satisfaction values in term of tensile and yield strength (Figs. 11, 12). Impact energy of tested duplex steels reaches from 87 to 99J for compositions based on austenitic powder however for composition based on ferritic powder shows the highest values, 151J of impact energy was measured for composition (C).

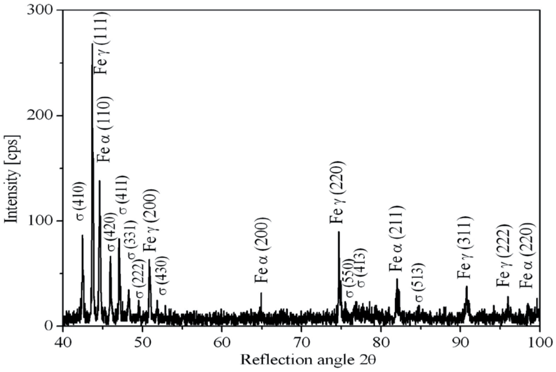

Fig. 9. X-ray diffraction pattern of sintered duplex steel, composition (A) slow cooled from sintering temperature

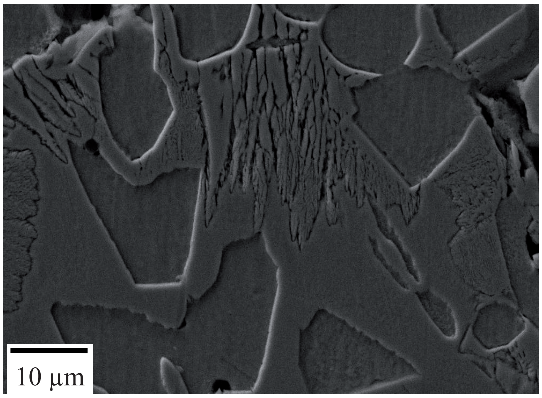

Fig. 10. Sigma phase precipitate in microstructure of composition (A) slow cooled from sintering temperature

Obtained results are in accordance with quantity rate of austenite and ferrite in the microstructure. Tensile test analysis shows, that the highest tensile strength Rm=652 MPa has been achieved for steel obtained by mixing both austenitic and ferritic powders in equal amounts. Sintered steels based on ferritic powder X6Cr13 achieved optimal results in case of tensile strength and elongation. It must be noted that elongation of all produced steels is in the rage of 3% to 7% thus proves greater sintering. Increase of mechanical properties of sintered duplex stainless steels with increasing ferrite content may by explained due to solid solution hardening of Ni and Mo in the ferrite phase. The internal strain hardening between ferrite and austenite due to different coefficients of thermal expansion, and the new growing inter-diffusion zone at particles boundary cause increase of tensile strength and hardness.

In the case of sintering cycle with slow cooling after sintering lower values of mechanical properties were achieved, due to precipitation of hard and brittle intermetallic sigma phase.

In the case of mixture (E) slow cooled after sintering cycle an increase was measured. The tensile strength of this composition rise about 10 MPa and the yield strength about 180 MPa what can by connected with more circular pore morphology in the microstructure which also result in higher elongation of sample during tensile test.

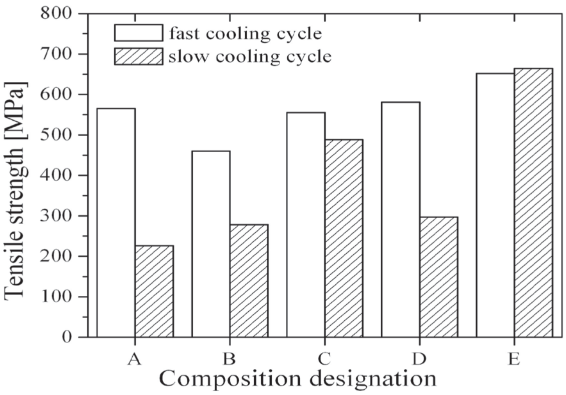

Fig.11. Tensile strength of analyzed sintered duplex steels

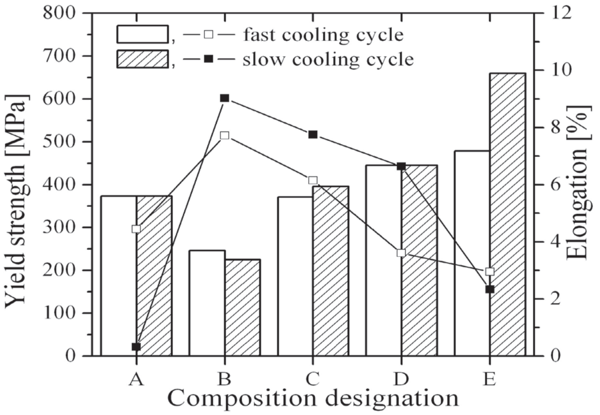

Fig. 12. Yield strength and elongation of analyzed sintered duplex steels

Performed fractography analysis demonstrates that fracture surfaces of all steels are a mixed type of ductile and brittle fracture. Fracture surfaces are composed of wide and deeper dimples, in case of composition (E) dimples are smallest and shallow. Slow cooled steels after sintering cycle demonstrate brittle fracture caused precipitation of sigma phase. For the sintering cycle wit slow cooling rate the presence of hard and brittle sigma phase precipitates cause the microstructure more sensitive to brittle fracture (Figs 13,14).

4. Conclusions

Applied producing method of sintered duplex stainless steels and used sintering cycle with fast cooling directly form sintering temperature proves his advantage in case of mechanical properties and additionally it seem to be very promising for obtaining a balanced duplex structure, also working with cycles easy to be introduced in industries. Introduction of pressurised nitrogen to achieve fast cooling rate directly from sintering temperature enabled precipitates free microstructure of sintered duplex steels in one sintering cycle.

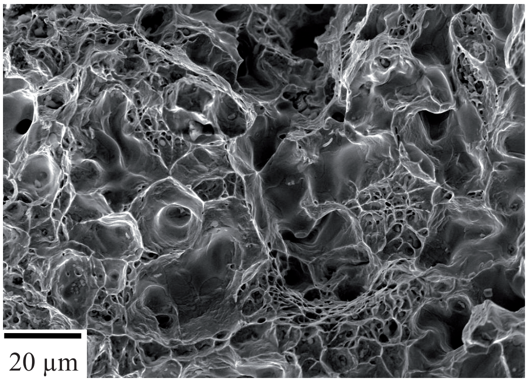

Fig. 13. Fracture surface of composition (A) sintered with fast cooling rate

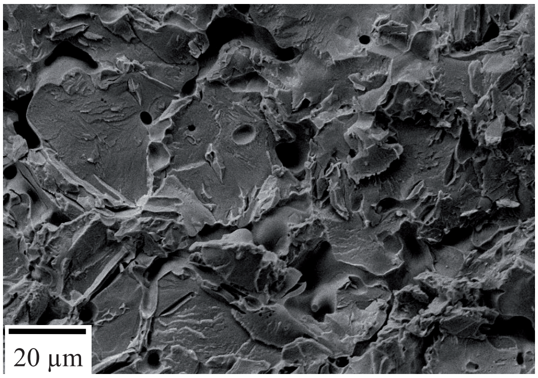

Fig. 14. Fracture surface of composition (A) sintered with slow cooling rate

According to achieved results, it was affirmed that applied sintering method as well as powder mixes preparation allows for manufacturing the sintered duplex steels with good mechanical properties which depends on austenite/ferrite ratio in the structure and elements partitioning between phases. Mechanical properties of sintered stainless steels are strictly connected with the density and the pore morphology present in the microstructure too.

Sinter-hardening treatment is expected to increase significantly over the next few years. The easier process, cost saving and better parts properties are some of the advantages. It must by noted that traditional sintering in hydrogen without cooling control of high alloyed powders may cause secondary phases precipitation, especially sigma. In these conditions after sintering, secondary treatment seems to by needed to obtain precipitate free structure influencing cost growth of a final product and causing higher usage of energy and technical gases which negatively react on the process performance.

The additions of alloying elements powders (promoting formation ferritic and austenitic phase) to master alloy powder, makes possible the formation of structure and properties of sintered duplex stainless steels. Sintered duplex steels obtained starting from austenitic and ferritic powders with admixture of elemental powders achieve lower mechanical properties when compared to composition obtained by mixing ferritic and austenitic powder in equal amounts.

Acknowledgements

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