Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 33
ISSUE 2
April
2009

Characteristic of vacuum sintered stainless steels

Z. Brytan [a,*], L.A. Dobrzański [a], M. Actis Grande [b], M. Rosso [b]
[a] Division of Materials Processing Technology, Management and Computer Techniques in Materials Science, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
[b] Department of Materials Science and Chemical Engineering, Politecnico di Torino, Alessandria Campus, Viale T. Michel 5, 15100, Italy
* Corresponding author: E-mail address: zbigniew.brytan@polsl.pl

Received 17.02.2009; published in revised form 01.04.2009

Materials

ABSTRACT

Purpose: In the present study duplex stainless steels were sintered in vacuum. using rapid cooling form the mixture of prealloyed and alloying element powders The purpose of this paper was to describe the obtained microstructures after sintering as well as the main mechanical properties of sintered stainless steels.
Design/methodology/approach: In presented work duplex stainless steels were obtained through powder metallurgy starting from austenitic 316L or ferritic 410L prealloyed stainless steels powders by controlled addition of alloying elements powder. Prepared mixes were sintered in a vacuum furnace in 1250°C for 1h. After sintering rapid cooling (6°C/s) using nitrogen under pressure was applied. Sintered compositions were subjected to structural examinations by scanning and optical microscopy and EDS analysis as well as X-ray analysis. Mechanical properties were studied through tensile tests and Charpy impact test.
Findings: It was demonstrated that austenitic-ferritic microstructures with regular arrangement of both phases and absence of precipitates can be obtained with properly designed powder mix composition as well as sintering cycle with rapid cooling rate. Obtained sintered duplex stainless steels shows good mechanical properties which depends on phases ratio in the microstructure and elements partitioning (Cr/Ni) between phases.
Research limitations/implications: Basing on alloys characteristics applied cooling rate and powder mix composition seems to be a good compromise to obtain balanced sintered duplex stainless steel microstructures.
Practical implications: Mechanical properties of obtained sintered duplex stainless steels structures are rather promising, especially with the aim of extending their field of possible applications.
Originality/value: The utilization of vacuum sintering process with rapid cooling after sintering combined with use of elemental powders added to a stainless steel base powder shows its advantages in terms of good microstructural homogeneity.
Keywords: Sinter-hardening; Powder metallurgy; Duplex stainless steel

Reference to this paper should be given in the following way:
Z. Brytan, L.A. Dobrzański, M. Actis Grande, M. Rosso, Characteristic of vacuum sintered stainless steels, Journal of Achievements in Materials and Manufacturing Engineering 33/2 (2009) 126-134.

1. Introduction

Sintered parts produced from prealloyed stainless steels powders are very attractive for wide branches of applications including automotive industry, household appliances, recreation and hand tools, hardware and many others. Stainless steels produced by powder metallurgy mainly single-phase stainless steels for many years have stable position on market of sintered components. 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 heated exhaust gas oxygen sensors. The automotive market introduces newly designed sintered parts in large amounts in produced cars. 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 by biggest users of powder metal exhaust system flanges in the world [1-3].

Attractive combination of corrosion resistance and mechanical properties of duplex stainless steels as well as the resistance to stress corrosion cracking superior than of standard austenitic steel contribute to wide interest of sintered duplex stainless steels. Usage of powder metallurgy as a cost effective and high performance technology and possibility of manufacturing products with dimensional stability and shape reproducibility causes the possibility to produce duplex stainless steels witch controlled mechanical properties and thus corrosion resistance [4,5]. Manufacturing of biphasic microstructure by sintering can take place in different manners. The sintering of atomized duplex powder exhibit in limited compressibility due to high alloying element concentration but the main advantage of this method is the possibility of introducing nitrogen in alloy ensuring higher mechanical properties and corrosion resistance. Mixing of fully prealloyed single phase powders in adequate proportion result in well constituted bi-phase microstructure with good mechanical and corrosion properties. The main disadvantage of this method is strictly defined chemical composition of base powders what determines narrow range of final chemical composition. Some improve can by obtained mixing of prealloyed powders with single alloying elements like Si, Mn and Ni thus desired biphasic microstructures are form but the risk of formation of undesired secondary phases is still high [6]. In spite of powder mix preparation method the sintering conditions play decisive role, thus sintering in hydrogen with low cooling rate applied determined the formation of complex structures, with partially un-identified secondary phases. Proper duplex stainless steels structures may be obtained within a single sintering cycle through controlled addition of alloying elements promoting formation of austenite or ferrite to single-phase powders both ferritic and austenitic trying to predict the final structure on the bases of Schaffler's diagram [7-9]. Alloying element may be added in form of single elements or in combined form and the sintering cycle is done in vacuum at argon backfilling and nitrogen is under pressure is used to obtain rapid cooling rate directly from sintering temperature.

Sintered stainless steels, in order to achieve high mechanical properties must be must be sintered in high temperatures applying inert atmosphere. The other manner to obtain such properties is to the addition of element powders provoking density increase leading to density increase and thus enhancing of the mechanical properties and corrosion resistance [10-13]. Depending on chemical composition sintered duplex stainless steels must be cooled form sintering temperature with controlled cooling rate due to possibility of precipitations of brittle intermetallic sigma phase which highly negatively influence on stainless steel properties. The presence of this brittle phase reduces the ductility and produce chromium depleted areas leading to decrease of the corrosion resistance and toughness [14-18].

Sinter-hardening process used to sintering duplex stainless steels ensured the possibility of producing complex biphasic microstructure with controlled mechanical properties and corrosion resistance in one sintering cycle with no need of the additional heat treatments [19,20].

The main purpose of this study is the investigation on the basic mechanical properties and microstructures of different duplex stainless steels compositions manufactured from base powder of prealloyed single phase stainless steel and addition of alloying elements powders.

2. Experimental procedure

To produce sintered duplex stainless steel different compositions have been tested, using austenitic AISI 316L and ferritic AISI 410L as starting base water atomized prealloyed powders of Hoganas Corporation (Table 1). Stainless steels base powders were mixed with addition of alloying elements powders such as Cr (in form of ferrochromium powder Fe-Cr), Ni, Mo and Cu in the right quantity to obtain the chemical composition similar to biphasic one. The compositions designated as N1, C, N2, D were prepared admixing powders to ferritic 410L powder whereas mixtures N3, A and N4 basing on austenitic 316L powder (Table 2).

Chemical compositions of produced mixtures were placed in austenitic-ferritic area of the Schaeffler's diagram (Fig. 1) with different content of both phases. During premix preparation and prediction of the final structure based on Schaffler's diagram, naturally isothermal projected phase diagram of ternary Fe-Cr-Ni system [10] was taken in to consideration and the proper range of coexistence of austenite and ferrite was controlled.

Table 1.
Average composition of starting powders

Base powder		Elements concentration, wt. %						
EN10088	AISI	Ni	Cr	Si	Mn	Mo	C	Fe
X2CrNiMo17-12-2	316L	13	16.4	0.9	0.2	2.5	0.03	bal.
X6Cr13	410L	0.14	12.2	0.88	0.09	-	0.04	bal.

Table 2.
Chemical composition of investigated powder mixes

Base powders	Composition designation	Elements concentration, wt. %							Cr_E	Ni_E	$(Cr/Ni)_E$
		Ni	Cr	Si	Cu	Mn	Mo	C			
316L	N3	10.33	27.75	0,80	-	-	1,99	0.02	34.9	10.9	2.81
	A1	10.52	26.40	0.80	0.80	-	2.02	0.02	33.7	11.1	3.30
	N4	11.19	24.10	0.83	-	-	2.15	0.03	31.8	12.1	3.44
410L	N1	9.10	21.05	0.69	2.00	0.06	2.00	0.03	28.1	10.0	3.68
	C1	8.10	22.72	0.70	-	0.06	2.00	0.03	29.8	9.03	3.20
	N2	8.10	24.09	0.69	2.00	0.06	2.00	0.03	31.1	9.03	3.04
	D1	8.09	26.23	0.65	2.00	0.06	2.00	0.03	33.2	9.02	2.63

During composition preparation lubricant Acrawax was used in a quantity of 0.65 wt.%. Premixes were prepared in tubular mixer for 20 min. and then uniaxially compacted using a floating die at 700 MPa. The dewaxing process was performed at 550°C for 60 minutes in a nitrogen atmosphere. Samples were then sintered in a vacuum furnace with argon backfilling at temperature 1250°C for 60 min. After sintering rapid cooling were applied using nitrogen under pressure of 0.6 MPa with cooling velocity of 6ºC/s calculated in range of 1250-400°C,

Microstructure observations were carried out using light microscope and scanning electron microscopy equipped in EDS probe. Evaluations of the phase composition were made using Bragg/Brentano ARL X'TRA 48 X-ray diffractometer with the filtered copper lamp rays CuKα and an acceleration voltage of 40 kV and heater current of 40 mA were applied. The measurements were made in the diffraction 2θ angle range of 40 - 100°.

Densities were evaluated using the water displacement method. Mechanical properties were evaluated basing on the tensile test performed according to EN 10002-1 standard on samples prepared according to ISO 3928 standard and Charpy impact test were performed according to EN 10045. Vickers hardness test was carried out in order to determine HV50 value. Fracture analysis was also carried out on tensile tested samples.

3. Results and discussion

Analyzing density of prepared compositions (Fig. 2) the main conclusion may be drawn that the ferritic based mixtures shows higher sintered densities than obtained for austenitic base powder even when starting with green density values similar for both compositions. For the composition based on the austenitic powder 316L the highest sintered density 6.81g/cm^3 was measured for A1 composition even when it shows the lowest green density. The lowest level of sintered density of this set of samples was measured for N4 composition where the quantity of admixed elemental powders to master prealloyed stainless steel powder was the lowest (Fig. 3). Difference between green and sintered density is only about 0.07g/cm^3. Opposite situation take place in case of composition C1 where the quantity of admixed elemental powders is high thus result in increase of density from green 6.67g/cm^3 to sintered one 7.11g/cm^3. Sintered density increase with the increase of admixed elemental powders (Fe-Cr). Analysing the chromium/nickel equivalent ratio $(Cr/Ni)_E$ of prepared compositions revealed that the maximum increase of density occur for $(Cr/Ni)_E$ =3.2-3.3.

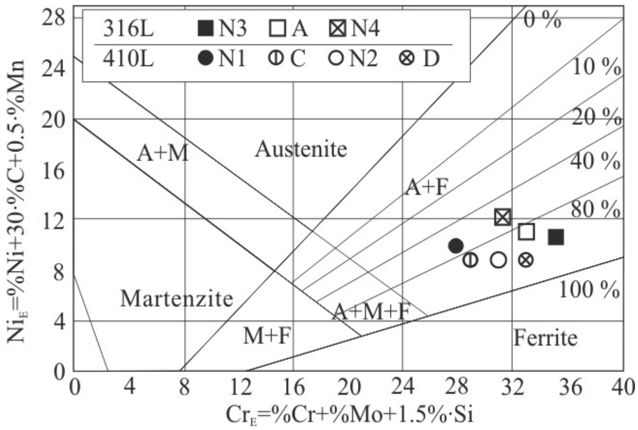

Fig. 1. Schaeffler's diagram, where the marked points determine the forecast microstructure of the prepared compositions

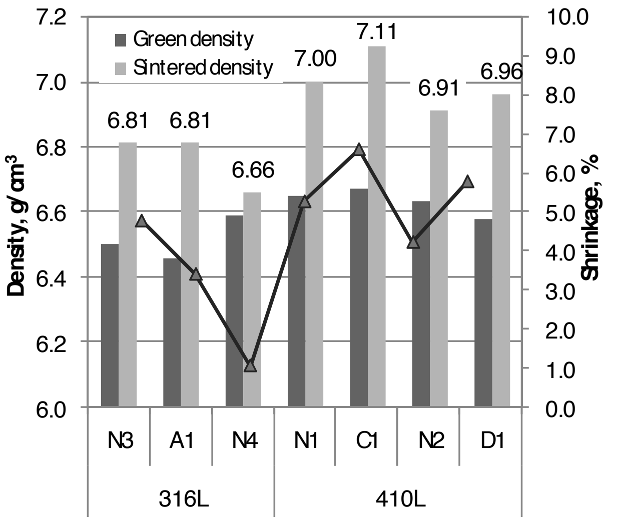

Fig. 2. Green and sintered density of studied powder mixes

Furthermore, increased sintered density result in high shrinkage (Fig. 2) of stainless powder mixes, what can by attributed to enhanced reactivity of ferritic powder when compared to austenitic powder and addition of elementals powder producing liquid phase during sintering stage.

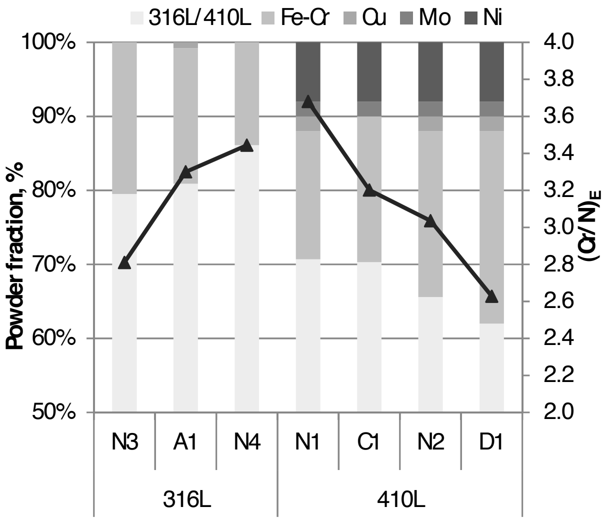

Fig. 3. Powder fraction and $(Cr/Ni)_E$ ratio of prepared mixes

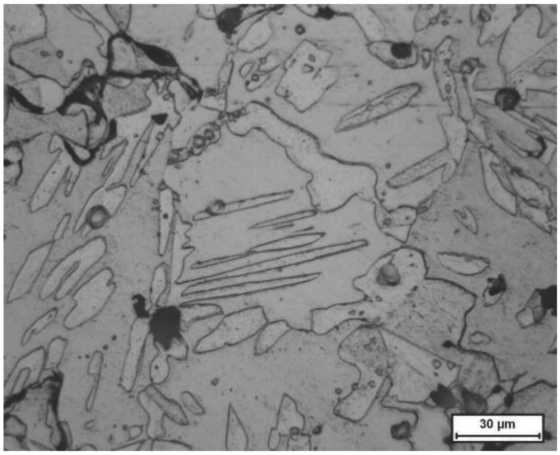

Fig. 4. Microstructure of composition N3

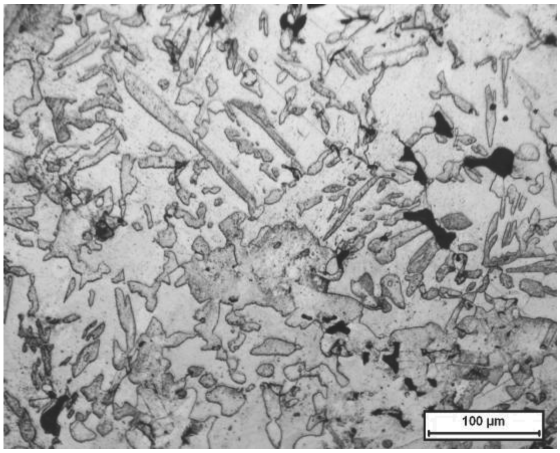

Fig. 5. Microstructure of composition C1

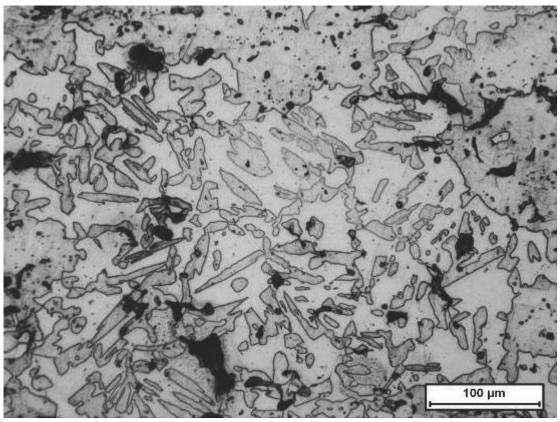

Fig. 6. Microstructure of composition N1

The study of the microstructures of the sintered stainless steels reveals bi-phase microstructure with a heterogeneous distribution of both phases (Figs. 4-6). Applied sintering cycle following with rapid cooling directly from sintering temperature enabled correct bi-phase - duplex microstructure formation without no precipitations of intermetallic phases. Microstructures of sintered stainless steel based on austenitic 316L powder is a mixture of ferrite and austenite, in case of compositions N3 and A1 in austenitic phase twined grains can be seen and austenite is uniformly distributed with ferritic grains. The microstructure of composition N4 present no uniform distribution of both phases. In this case the fraction of additional alloying powders was not sufficient to crate proper duplex microstructure and in the matrix of austnite relatively large clusters of ferritic phase are present (Fig. 7). Metallographic observations of ferritic 410L base powder compositions shows also proper duplex mixture with no presence of secondary precipitations. The increase of admixing powder quantity in compositions from N1 to D1 cause formation of austenitic phase in ferritic matrix. The microstructure of those composition is well formed and individual grains are fine and well mixed and the presence of lenticular austenite (Fig. 8) in ferritic matrix was reveled.

The phase composition of the sintered stainless steels was analysed by X-ray diffraction (Fig. 9). Figure 10 shows XRD patterns for the as-sintered composition. X-ray analysis revelled peaks come from the austenitic and ferritic phase. Studding the diffraction lines of particular phase and its content (Table 3) can by noted that for N4 composition even when predicted chemical composition should be the duplex microstructure it is still not proper formed and predominant reflections of ferritic phase are present. In the case of ferritic 410L base powder compositions the proper duplex microstructure is created more easily but the Schaeffler's diagram values must be simply shifted down to achieve good agreements with measured phase quantities. Performed analyses do not demonstrated any other secondary phases like sigma phase, carbides or nitrides precipitates in this sintering conditions.

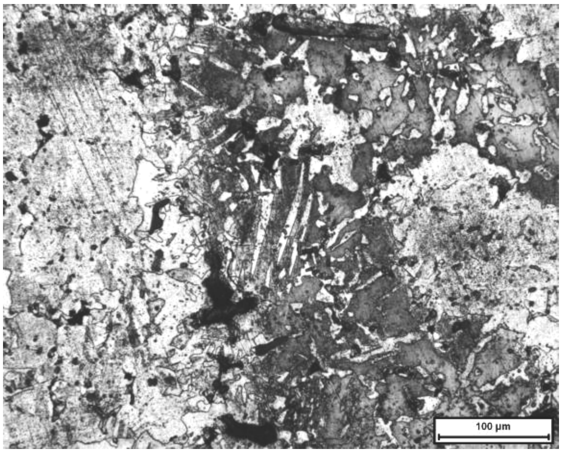

Fig. 7. Microstructure of sintered duplex stainless steel composition N3

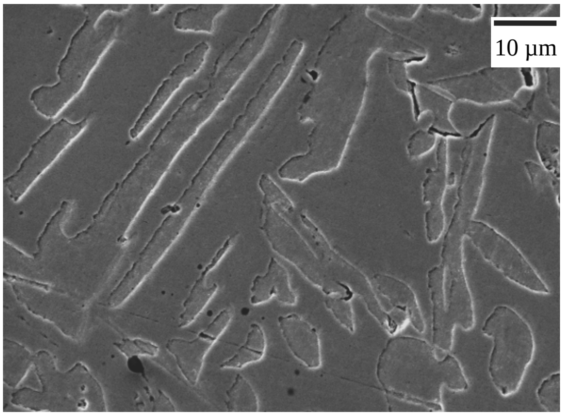

Fig. 8. Microstructure of sintered duplex stainless steel composition N2

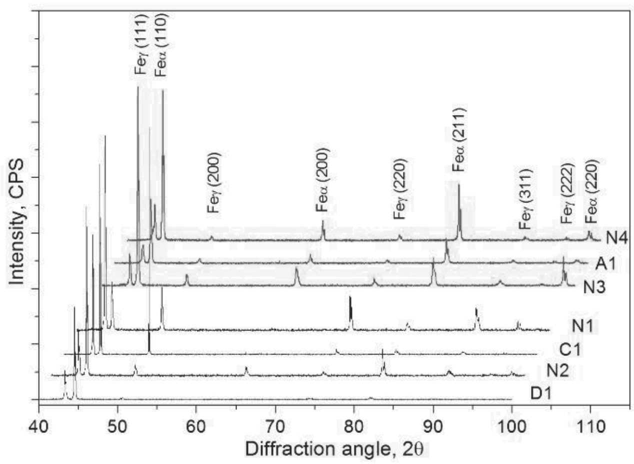

Fig. 9. X-ray diffraction patterns of studied sintered stainless

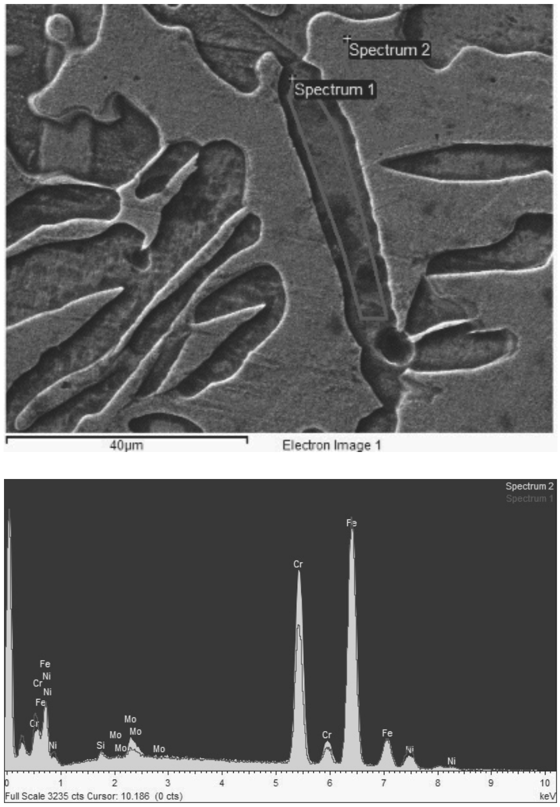

Fig. 10. Distribution of alloying elements in austenitic (spectrum 1) and ferritic region (spectrum 2) - composition D1

Table 3.
Phase quantity in the microstructure of sintered duplex stainless steels

Phase quantity, %	Composition designation						
	N3	A1	N4	N1	C1	N2	D1
Austenite	25	26	19	67	54	33	26
Ferrite	75	74	81	33	46	67	74

During scanning microscopy observations the EDS analysis were performed on phases present in microstructure (Table 4). Obtained results reveled that the concentration of ferrite former elements like Cr and Mo in ferrite region is higher wile concentration of Ni is lower than in austenitic region. The element partitioning between both phases is consistent with the stabilizing effect of each element on the respective phase. Main conclusion deriving form microstructures of manufactured duplex stainless steels is the possibility of application sinter-hardening process with rapid cooling as well as powder mixtures preparation to ensure desired balance between phase concentration and elements partitioning between phases. The addition of alloying element powders (promoting formation of ferritic and austenitic phase) to master prealloyed powder, makes possible the formation of microstructures and therefore increase of sintered duplex stainless steels properties.

Table 4.
Results of EDS analysis of selected austenitic and ferritic region in studied sintered duplex stainless steel

Base powders	Composition	Phase	Elements concentration, wt. %				Cr/Ni
			Ni	Cr	Si	Mo	
316L	N3	γ	8.15	20.70	0.61	1.70	2.54
		α	5.76	32.47	0.78	3.35	5.64
	A1	γ	9.66	25.30	0.78	1.76	2.62
		α	4.95	33.38	0.90	3.67	6.74
	N4	γ	9.36	25.15	0.89	2.16	2.69
		α	4.87	32.79	0.95	3.86	6.73
410L	N1	γ	6.69	23.00	0.61	2.90	3.44
		α	3.50	28.15	0.97	4.79	8.04
	C1	γ	6.63	22.53	0.75	2.07	3.40
		α	3.63	28.46	0.81	3.84	7.84
	N2	γ	7.23	24.29	0.77	3.01	3.36
		α	3.77	32.71	0.60	3.74	8.68
	D1	γ	8.98	23.02	0.86	1.67	2.56
		α	4.56	30.64	0.70	3.69	6.72

Furthermore, addition of element like copper results in liquid phase formation during sintering and through it influences the growth of sinterability due to faster mass transport. This is evident for compositions containing this alloying element with reason of higher sintered density when compared to sintered duplex stainless steels without this addition.

The hardness measurements of studied materials are in consistence with individual phase quantity where the increase of ferrite content result in hardness increase (Fig. 11).

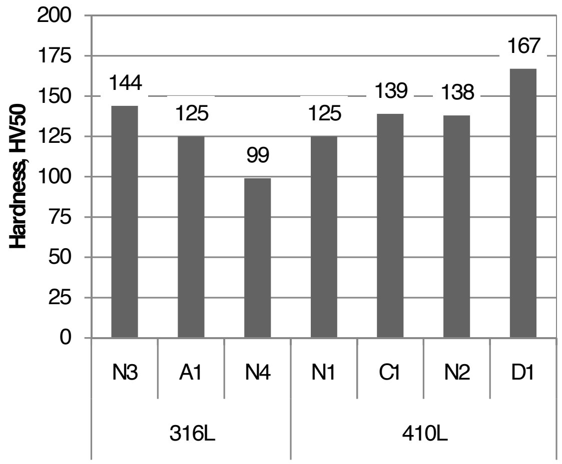

Fig. 11. Hardness of sintered composition

Vacuum sintered duplex stainless steels with rapid cooling directly from sintering temperature shows good mechanical properties in term of tensile and yield strength as well as elongation values. Sintered duplex stainless steels compositions based on 316L base powder (Fig. 12) exhibits tensile strength R_m=530 MPa for N3 composition with yield strength of $R_{p0,2}$=380 MPa and elongation A=7.7%. The highest tensile strength for ferritic 410L base powder compositions (Fig. 13) were obtained for C1 mix where R_m=500 MPa and $R_{p0,2}$=300 MPa and elongation reach A=16%. Obtained mechanical properties (Fig. 14) strictly depend on quantity rate of austenite and ferrite in the microstructure of analyzed steels. Improved mechanical properties of sintered duplex stainless steels with increased ferrite content may by explained due to solid solution hardening of ferrite phase with Ni and Mo. Furthermore, the internal strain hardening between both phases cause increase of tensile strength and hardness.

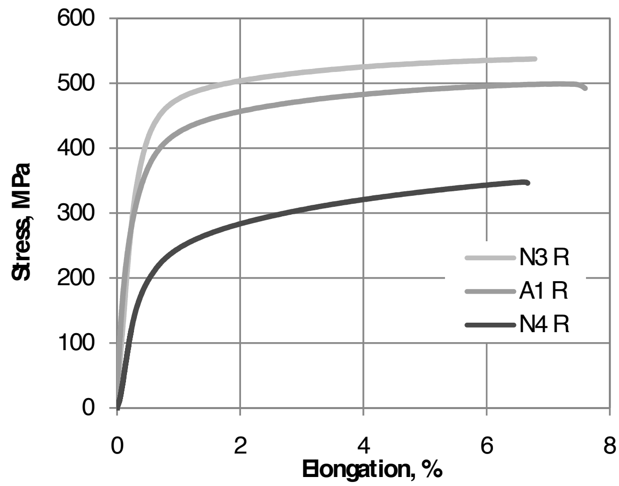

Fig. 12. Tensile strength of sintered duplex stainless steel based on the austenitic 316L stainless powder

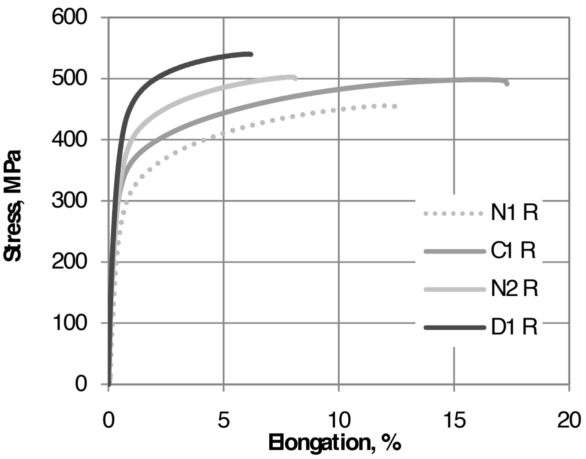

Fig. 13. Tensile strength of sintered duplex stainless steel based on the ferritic 410L stainless powder

Studied compositions submitted to Charpy impact test showed impact energy values from 34 to 47 J for compositions based on austenitic powder and for composition based on ferritic one the higher values were obtained, from 44 do 54 J with exception of composition C1. For this mixture the higher value of 118 J of impact energy was measured. Fractography analysis demonstrated that fracture surfaces of all compositions are ductile type fracture and they clearly underlines the presence of dimples throughout all examined surface (Fig. 15). In case of samples C1 the highest value of impact resistance can be attributed to the approximately exact bi-phase microstructure as well as the highest density among studied compositions (Fig. 16).

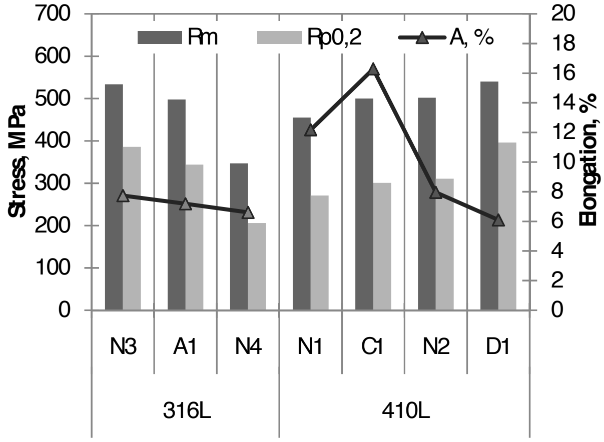

Fig. 14. Average mechanical properties of studied sintered duplex stainless compositions

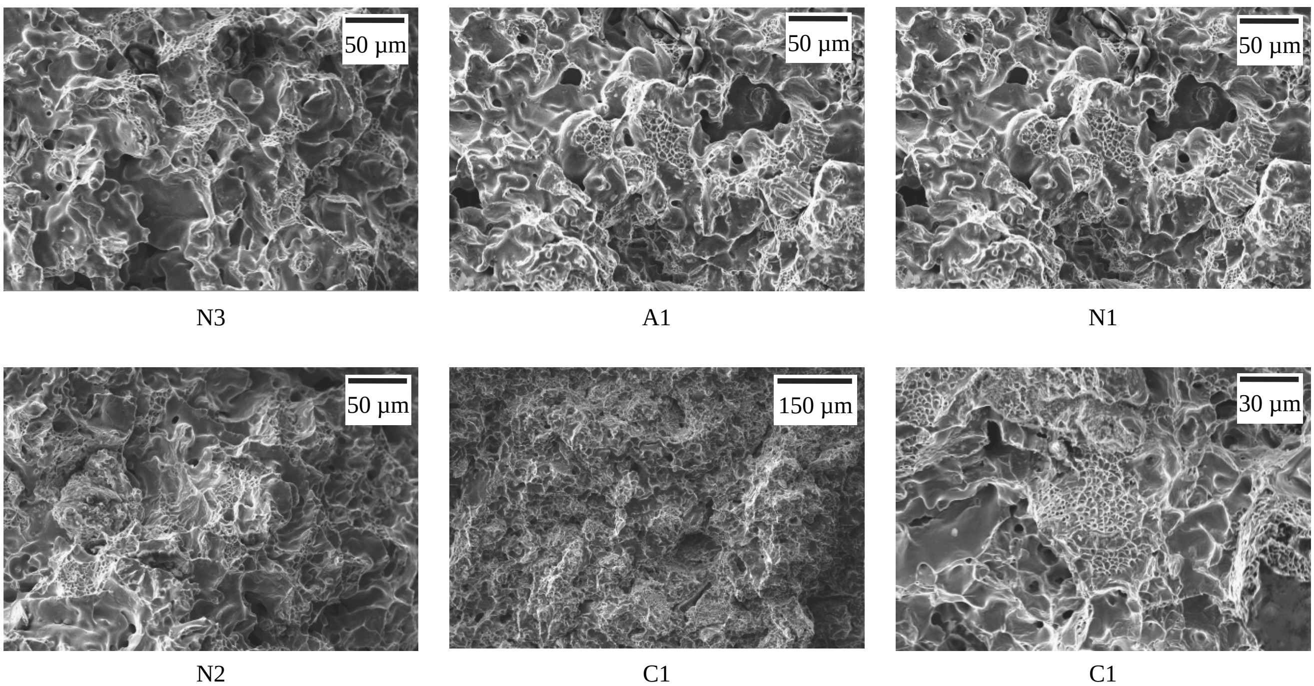

Fig. 15. Fracture surfaces of studied sintered stainless steels sintered in vacuum and rapid cooled directly from sintering temperature

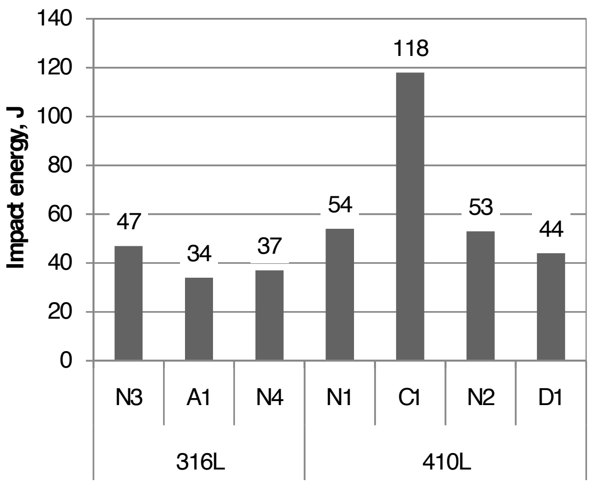

Fig. 16. Average toughness values for examined powder mixes

4. Conclusions

It has been demonstrated that bi-phasic austeno-feritic structures with regular arrangement of both phases and no presence of precipitates can be obtained through a properly designed powder mixture and sintering cycle in vacuum. It was shown that use of ferritic stainless steel powder for manufacturing the duplex microstructures gives higher sintering density than using austenitic stainless steel powder.

Mechanical properties of the structures are rather promising, especially with the aim of extending the field of applications of sintered duplex stainless steels. Nevertheless attention has to be paid to the sintering step and most of all for the following cooling stage. Among analysed compositions the best mechanical properties reach C1 composition obtained basing on ferritic 410L powder where the balance of austenite and ferrite was achieved and the tensile strength value was 500 MPa with elongation of 16%. The impact energy of this composition was about 118 J whereas for rest composition maximally 50 J was obtained. Mechanical properties of produced compositions strictly depend on the quantities of individual phase components in the microstructure and with the increase of ferritic phase content in microstructure increase the tensile and yield strength as well as hardness. Whereas ductility and impact energy is accompanied by increase of austenitic phase content in sintered duplex microstructure.

Studied compositions shows the proper sintered duplex microstructure and the highest mechanical properties increase where the chromium/nickel equivalent ratio (Cr/Ni)E is about 3.2-3.3. Nevertheless, the correlation between powder fractions and formation of a complex duplex microstructure involve an additional studies in the future.

References

[1] P.K. Samal, J.B. Terrell, Mechanical properties improvement of PM 400 series stainless steels via nickel addition, Metal Powder Report December 2001 (2001) 28-34.

[2] A.J. Rawlings, H.M. Kopech, H.G. Rutz, The effect of service temperature on the properties of ferritic P/M stainless steels, Proceedings of the International Conference "Powder Metallurgy & Particulate Materials" PM2TEC'97, Chicago, USA, 1997.

[3] M. Rosso, M. Actis Grande, D. Ornato, Sintering of duplex stainless steels and their properties, Powder Metallurgy Progress 2 (2002) 10-17.

[4] F. Velasco, A. Bautista, A. González-Centeno, High-temperature oxidation and aqueous corrosion performance of ferritic, vacuum-sintered stainless steels prealloyed with Si, Corrosion Science 51 (2009) 21-27.

[5] C. Garcia, F. Martin, P. de Tiedra, Y. Blanco, J.M. Ruiz-Roman, M. Aparicio, Electrochemical reactivation methods applied to PM austenitic stainless steels sintered in nitrogen–hydrogen atmosphere, Corrosion Science 50 (2008) 687-697.

[6] K. Sikorski, A. Szymańska, D. Kowalczyk, J. Kazior, K.J. Kurzydłowski, Effect of silicon addition on the microstructure and mechanical properties of 316L austenitic stainless steel, Proceedings of the European Powder Metallurgy Association, Euro PM,2005, vol. 1, 2005, 419-424.

[7] L.A. Dobrzański, Z. Brytan, M. Actis Grande, M. Rosso, E.J. Pallavicini, Properties of vacuum sintered Duplex Stainless Steels, Journal of Materials Processing Technology 157-158 (2004) 312-316.

[8] L.A. Dobrzański, Z. Brytan, M. Actis Grande, M. Rosso, Sintered Duplex Stainless Steels Corrosion Properties, Materials Science Forum 534-536 (2007) 721-724.

[9] M. Actis Grande, D. Ugues, L.A. Dobrzański, Z. Brytan, M. Rosso, Properties of vacuum sintered duplex stainless steels, Proceedings of the Powder Metallurgy World Congress and Exhibition, PM'2004, Vienna, 2004, vol. 3, 395-399.

[10] M. Campos, A. Bautista, D .Caceres, J. Abenojar, J.M. Torralba, Study of the interfaces between austenite and ferrite grains in P/M duplex stainless steels, Journal of the European Ceramic Society 23 (2003) 2813-2819.

[11] P. Datta, G.S. Upadhyaya, Sintered duplex stainless steels from premixes of 316L and 434L powders, Materials Chemistry and Physics 67 (2001) 234-242.

[12] J. Kazior, T. Pieczonka, A. Molinari, Properties of AISI 316L, AISI 434L and duplex stainless steel, Proceedings of the 8th International Scientific Conference „Achievements in Mechanical and Materials Engineering" AMME'1999, Gliwice–Rydzyna–Rokosowo–Pawłowice, 1999, 289-293.

[13] M. Campos, P. Sarasola, J.M. Torralba, Sintering evolution of duplex stainless steels obtained from austenitic and ferritic stainless steels powders mixtures, Proceedings of the 9th International Scientific Conference „Achievements in Mechanical and Materials Engineering" AMME'2000, Gliwice–Sopot–Gdańsk, 2000, 83-86.

[14] L.A. Dobrzański, Z. Brytan, M. Actis Grande, M. Rosso, Corrosion resistance of sintered duplex stainless steel evaluated by electrochemical method, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 317-320.

[15] H. Krztoń, D. Kolesnikow, J. Paducha, R. Molenda, Processing and properties of sinters prepared from 316L steel nanopowders, Journal of Achievements in Materials and Manufacturing Engineering 21/2 (2007) 73-76.
[16] C. Garcia, F. Martin, Y. Blanco, M.P. de Tiedra, M.L. Aparicio, Corrosion behaviour of duplex stainless steels sintered in nitrogen, Corrosion Science 51 (2009) 76-86.
[17] S.S. Panda, V. Singh, A. Upadhyaya, D. Agrawal, Sintering response of austenitic (316L) and ferritic (434L) stainless steel consolidated in conventional and microwave furnaces, Scripta Materialia 54 (2006) 2179-2183.
[18] C.J. Munez, M.V. Utrilla, A. Urena, Effect of temperature on sintered austeno-ferritic stainless steel microstructure, Journal of Alloys and Compounds 463 (2008) 552-558.
[19] M. Rosso, M. Actis Grande, High density sintered stainless steels with improved properties, Journal of Achievements in Materials and Manufacturing Engineering 21/2 (2007) 97-102.
[20] L.A. Dobrzański, Z. Brytan, M. Actis Grande, M. Rosso, Properties of duplex stainless steels made by powder metallurgy, Archives of Materials Science and Engineering 28/4 (2007) 217-223.