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TWO-STEP BORIDES CRYSTALLIZATION PROCESS AFTER SINTERING OF POWDER OF BORON MODIFIED AISI 316L AUSTENITIC STAINLESS STEEL

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ABSTRACT: Powder of AISI 316L austenitic stainless steel modified with 0,3 wt.% elemental boron was sintered in dry hydrogen atmosphere at temperature of 1240°C. Microstructures were analyzed by means of optical and scanning electron microscope. Chemical composition of phases was determined by EDS. Obtained results were used as a basis for thermodynamic simulation of crystallization process using Scheil-Gulliver Modified solidification model Thermo-Calc software program. On the basis of experimental work it was concluded that two-step crystallization of borides during cooling from sintering temperature take place.
KEYWORDS: austenitic stainless steel, microstructure, thermodynamic simulation

INTRODUCTION

Enhancing of the sintering process of parts made from stainless steels powders is an interests object of modern industry. Necessity of using high purity sintering atmospheres and high sintering temperatures during sintering process of stainless steels causes this process quite expensive. Because of that implementing finishing processes in order to rise density (e.g. forging) or close opened porosity makes the process less economical that is why many researchers [1, 2, 3] investigates the liquid state sintering process for stainless steels powder as an alternative to obtained full density sintered material.

There are many elements suitable to activate sintering process of ferrous alloys [4] but one of the most promising is the boron. Boron induces eutectic reaction with iron matrix and creates an eutectic liquid [1] which greatly improves final density of sinters. Unfortunately, after sintering process an eutectic liquid remains on grain boundaries as solidified brittle phase which significantly lowers mechanical properties of sintered part. Understanding the solidification process and identification of precipitated phases may provide an answer how to modify chemical composition of sinter to induce borides spheroidization instead creating undesired borides network surrounding matrix grains.

EXPERIMENTAL PROCEDURE

Powder of AISI 316 L~~HD~~ stainless steel provided by Höganäs AB was used as a base powder. Elemental boron was added by 24-hour mixing in Turbula® mixer in amount of 0.3wt.%. Ø20x5mm green compacts were cold pressed under 600MPa and sintered in pure dry hydrogen in Nabertherm P330 furnace according to temperature profile: heating with 10°C/min rate up to 1240°C, 30mins of isothermal sintering and cooling with 20C°/min rate.

Metallographic cross-section was obtained by means of grinding and polishing by alumina powder water suspension. Microstructures were obtained by etching in Villel's reagent for stainless steels. Calorimetric tests were carried out according to the same temperature profile as Ø20x5mm samples but in pure argon atmosphere on STA 409 CD (Netzsch) calorimeter. Thermodynamic simulations were performed using Thermo-Calc software program equipped with TCFE6 database. Chemical compositions of borides were estimated using EDS technique on JEOL JSM-820 scanning electron microscope.

RESULTS AND DISCUSSION

Examination of microstructure (Figure 1) revealed presence of precipites on grain boundaries what was reported earlier by other authors [1-3]. Also an extensive grain growth was observed what is the consequence of liquid phase sintering of stainless steel powder activated by boron addition.

Lozada and Castro [3] confirmed by TEM examination a presence of M_2B tetragonal borides after sintering AISI 316L modified with elemental boron but calorimetric tests revealed two overlapping

endothermic peaks which maxima were estimated at 1196°C and second one at 1181°C (Figure 2). Such an observation suggests that eutectic liquid solidifies as two separate phases.

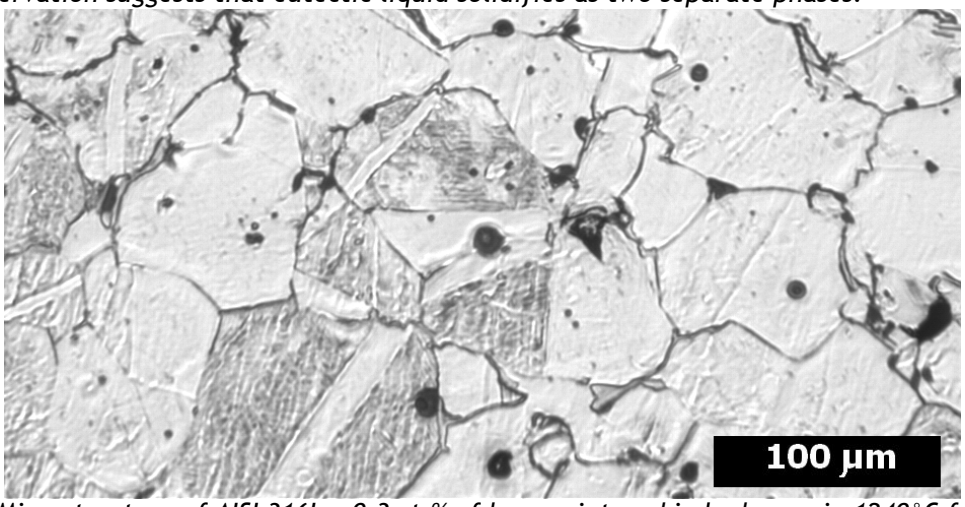

Figure 1. Microstructure of AISI 316L + 0.3wt.% of boron sintered in hydrogen in 1240°C for 30mins.

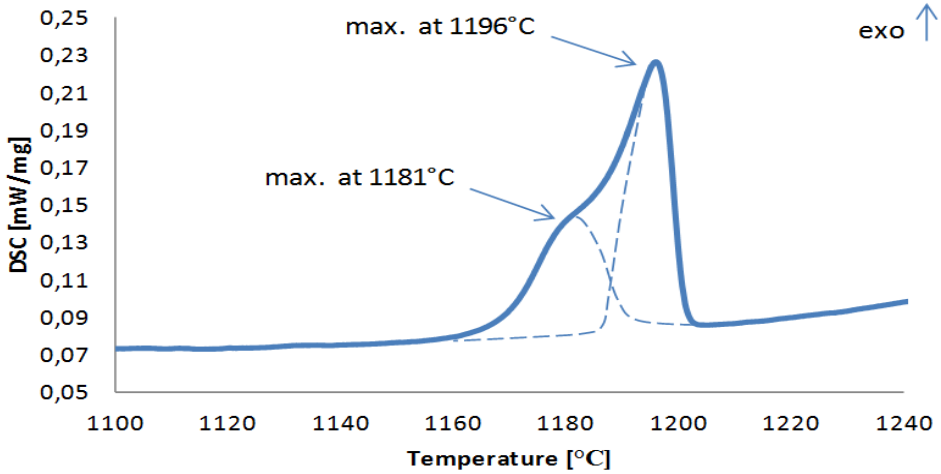

Figure 2. Selected part of DSC cooling stage

In order to confirm its presence the EDS examination was carried out. Figure 3 presents EDS examination points.

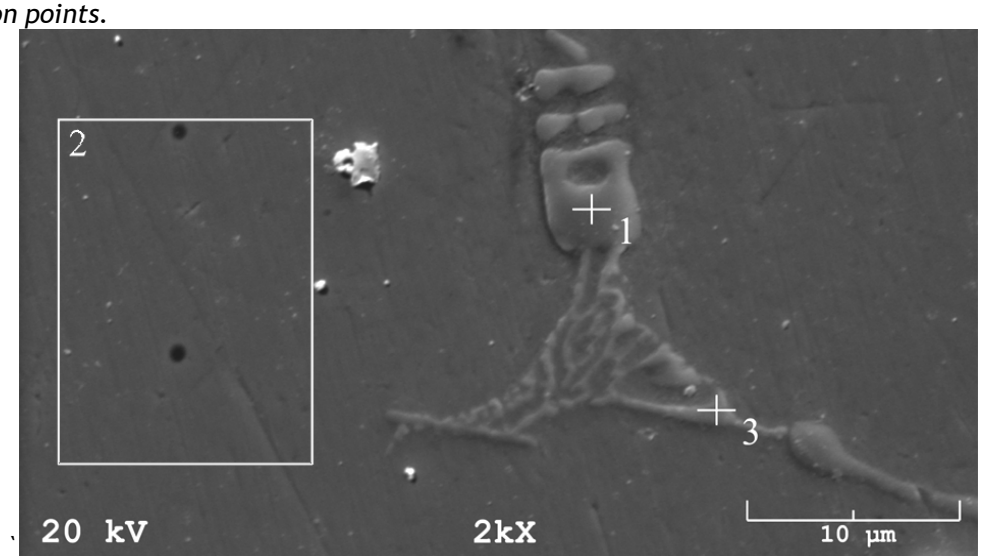

Figure 3. EDS examination points

Chromium-rich and molybdenum-rich precipitates were found in the microstructure. Morphology of both precipitates differs significantly - while chromium-rich precipitations are bulk and assumes oval shapes, the molybdenum-rich precipitations are thin, scattered and placed between Cr-rich precipitations. In some points both smoothly replace each other but mostly just exist neighboring. It has been noticed that Cr-rich precipitations usually locates in junction point of three neighboring grains while Mo-rich borides usually are located on grain boundaries. Tab. 1 presents precise results of EDS measurements.

Table 1. Results of EDS measurements:
1 - chromium-rich precipitation; 2 - matrix; 3 - molybdenum-rich precipitation

1			2			3		
Elt.	Conc. [wt. %]	Error 2-sig	Elt.	Conc. [wt. %]	Error 2-sig	Elt.	Conc. [wt. %]	Error 2-sig
Si	0,274	0,179	Si	1,041	0,270	Si	0,242	0,163
Cr	**53,636**	0,79	Cr	15,222	0,236	Cr	24,275	0,536
Fe	35,069	0,81	Fe	67,382	0,376	Fe	31,341	0,717
Ni	1,329	0,352	Ni	12,255	0,482	Ni	4,048	0,393
Mo	9,691	0,618	Mo	4,100	0,691	Mo	**40,095**	0,997
	100			100			100	

Due to necessity of identification observed phases thermodynamic simulation using Thermo-Calc software was performed. Scheil-Gulliver Modified model [5] was applied to simulate solidification examined material. Figure 4a shows two energetic reactions - first one, responsible for M_2B crystallization at 1250°C and second one and second at 1170°C originated from solidification of Cr_2B borides. Recorded temperatures of peaks maxima differ from those obtained using simulation - this is an effect of limited toleration of boron element in TCFE6 database. On the other hand, simulation predicted confirmed presence of two different borides.

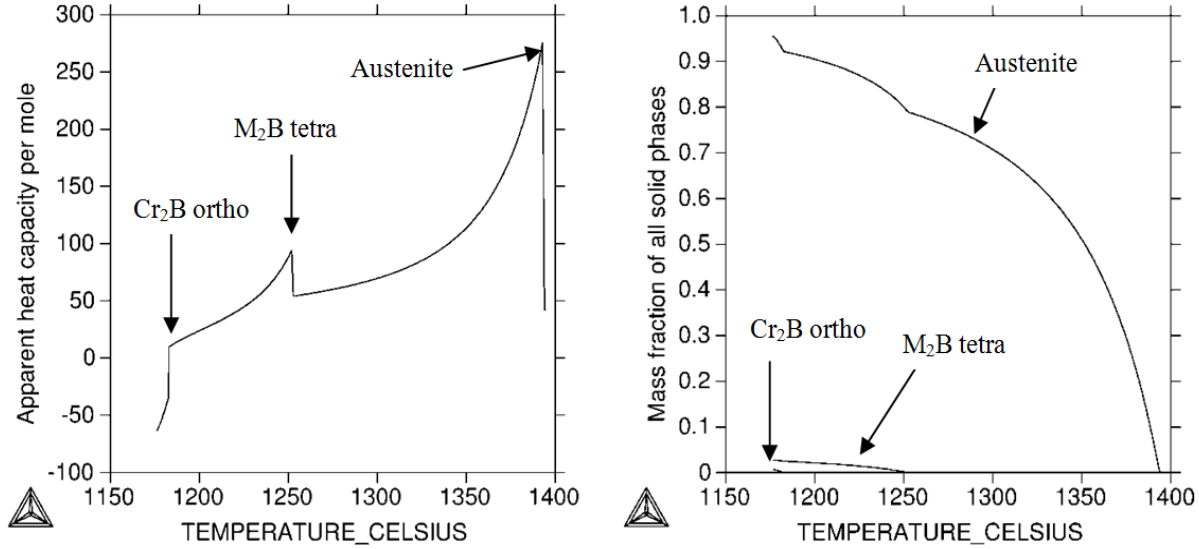

Figure 4. a) Apparent heat capacity changes along with temperature change;
b) Mole fraction of solids along with temperature change

Figure 4b presents simulation of mole fraction of solidified particular phases. Form plot emerges that of M_2B precipitates in much wider temperature range than Cr_2B - that is why it has enough time to spheroidize oppositely to Cr_2B which has only a short period of time to solidify what is the main reason of its scattered shape.

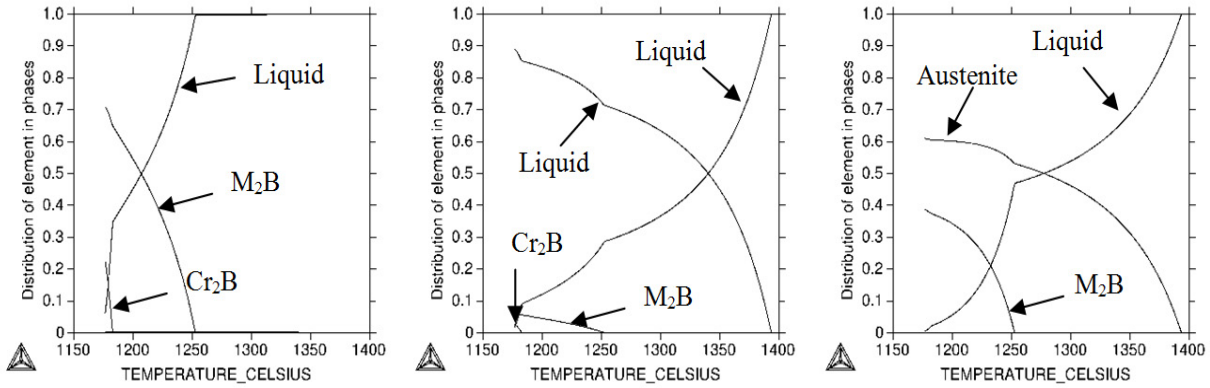

Figure 5. Distribution of crucial elements in particular solidified phases:
a) Boron; b) Chromium; c) Molybdenum.

As emerges from Figure 5a boron do not solute [6] in iron matrix so it locates almost completely in borides what agrees with binary phase diagram Fe-B [7]. Figure 5b shows that approximately 10% of whole chromium content was consumed for borides formation - it may lower the corrosion resistance of sintered stainless steel specimens but as it was investigated [1] in fact corrosion resistance rises as the consequences of almost full densifications of sintered compacts. Figure 5b presents data suggesting that almost 40% of molybdenum in alloy is consumed by M2B formation. According to EDS analysis of matrix which do not confirms this (molybdenum is present in matrix) though total amount of borides in simulation seems to be overestimated and should be lower.

CONCLUSIONS

The solidification model of AISI 316L modified with 0.3wt.% of elemental boron was developed. Presence of two different borides has been found and it was identified to be Cr_2B orthogonal and M_2B tetragonal by means of DSC, EDS and Thermo-Calc simulation. Those new information gives a new indication how to modify chemical composition of boron alloyed AISI 316L austenitic stainless steel powder. Further modifications or thermal operation may lead to spheroidization of M_2B borides and to rise of mechanical properties in this way.

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