Materials Science Forum *Online: 2007-01-15*
ISSN: 1662-9752, Vols. 534-536, pp 661-664
doi:10.4028/www.scientific.net/MSF.534-536.661

Development of PM Stainless Steels with Improved Properties through Liquid Phase Sintering

C. Tojal [a], T. Gómez-Acebo [b] and F. Castro [c]

Centro de Estudios e Investigaciones Técnicas de Gipuzkoa (CEIT)
Pº de Manuel Lardizabal 15, 20018, San Sebastián, Spain.

[a] ctojal@ceit.es, [b] tgacebo@ceit.es, [c] fcastro@ceit.es

Keywords: Austenitic, Boron, Master Alloys, Tensile Properties, High Density.

Abstract. The use of boron for successfully obtaining high density PM stainless steels with improved mechanical properties and corrosion resistance is presented. Boron is added as part of master alloys which have been specifically designed to provide the formation of wetting liquid phases with excellent characteristics for producing controlled densification and alloying of 316L and 304L austenitic stainless steels. The as-sintered density and properties of these alloys is determined by the amount of master alloy, the chemical composition of the stainless steel powder, the sintering temperature and time. The microstructural development and alloy homogenisation are determined by the chemical composition of the Fe-based powder and the chemical reactions taking place between the basic powder and the master alloy particles during high temperature sintering. The use of this master alloy is shown to lead to stainless steels with outstanding combinations of strength and ductility. The influence of alloying and the sintering conditions on the final microstructure, density, corrosion resistance and tensile properties is also discussed.

Introduction

PM stainless steels are currently used in several applications (*1-3*) and their use is increasing associated to requirements of high corrosion resistance (*1, 4-7*). Nevertheless, they exhibit lower corrosion resistance than their wrought counterparts due to porosity and processing conditions (*5, 8*). Solid solution strengthening in these highly alloyed powders imposes a severe limitation on the green density achieved after die pressing. Consequently liquid phase sintering is an attractive method for obtaining an improved performance. Boron is an effective sintering enhancer for obtaining high density iron and iron-alloys (*9-11*). Even small additions of this element produce a noticeable increase on the densification rate upon formation of a liquid phase (*12-14*). The permanent liquid forms at relatively low temperatures exhibiting excellent wetting characteristics and an extremely low solubility in the solid (*15, 16*). Due to these attractive characteristics the use of boron has been actively investigated for sintering stainless steels (*16-26*) although detrimental effects on mechanical properties have also been reported (*27, 28*). In the present work the results obtained after using a set of recently developed boron-containing master alloys, called CEITALOY HD and CEITALOY HE (*29*), for sintering stainless steels is presented. The high density stainless steels presented here show outstanding mechanical properties and improved corrosion resistance in comparison to previously used PM materials.

Experimental procedure

The base stainless steel powders used in this research work are the 316L and 304L grades whose chemical compositions are summarised in Table 1. After blending with a fixed amount of CEITALOY HE or CEITALOY HD (*29*), which are two grades of a B-Fe-Si-Mn-Ni alloy, the powder mixtures were die pressed at 700 MPa to reach green densities of 6.6 and 6.7 for grades 304L and 316L respectively. The green compacts were subsequently sintered in dry hydrogen (DP better than -40ºC) for 1 hr at selected temperatures between 1210 and 1280ºC. The as-sintered microstructures, as well as the fracture surfaces obtained after tensile testing under MPIF standards, were characterised by optical and scanning electron microscopy.

Table 1.- Chemical composition of the base stainless steel powders.

Steel grade	Cr	Ni	Mo	Cu	Mn	Si	C	O	Fe
304L	19.0	11.25	-----	-----	------	0.75	0.02	0.24	Bal
316L	17.0	13.00	2.20	-----	0.20	0.80	0.02	0.24	Bal

Results and discussion

Since both master alloys produce a very similar densification response for the austenitic stainless steels powders used in this work, Figure 1 is included as an example to show the densification behaviour of a set of powder compacts containing a fixed amount of CEITALOY HE. As expected, higher sintering temperatures produce higher density levels due to the thermal activation of the system based on the intervention of dissolution-precipitation and shape accommodation mechanisms. In addition, it may also be realised that the temperature for densification-start is dependent on the grade of stainless steel used.

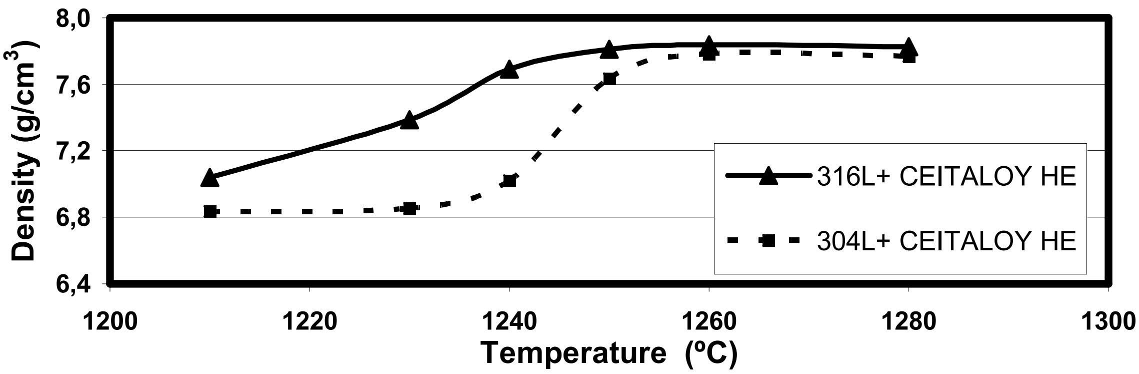

Figure 1.- Densification as a function of sintering temperature of powder mixtures based on stainless steels 316L and 314L and 3%wt additions of master alloy CEITALOY HE.

This behaviour is due to the difference in temperature for the formation of the persistent liquid phase in every alloy system. Such difference is caused, in turn, by the difference in temperature at which the complex borides, formed with distinct thermodynamic stability and chemical composition, are able to participate in the generation of the liquid. As noticed in Fig. 1 sintering of the 316L grade starts at lower temperatures than those for the 304L grade. This is due to the beneficial influence of molybdenum encouraging the generation of a liquid at lower temperatures. In total agreement with a previous report (*19*) it was observed that this liquid is generated by a eutectic reaction between the alloyed austenite and complex borides of the $(Fe,Cr,Mo)_2B$ type. In contrast, for the 304L grade which does not contain molybdenum, the borides intervening in the generation of the liquid are chromium rich causing a displacement of the eutectic reaction to a higher temperature.

As a result, according to detailed microstructural characterisation, involving x-ray mapping under the SEM it was observed that the final liquid formed in the 304L grade is Cr-rich, whereas for the 316L grade it also contains important amounts of Mo. Once the liquid is formed and during the holding period at the sintering temperature, the microstructural changes involve the spreading of the liquid, the smoothing of the chemical gradients, rounding of porosity and a certain amount of grain growth.

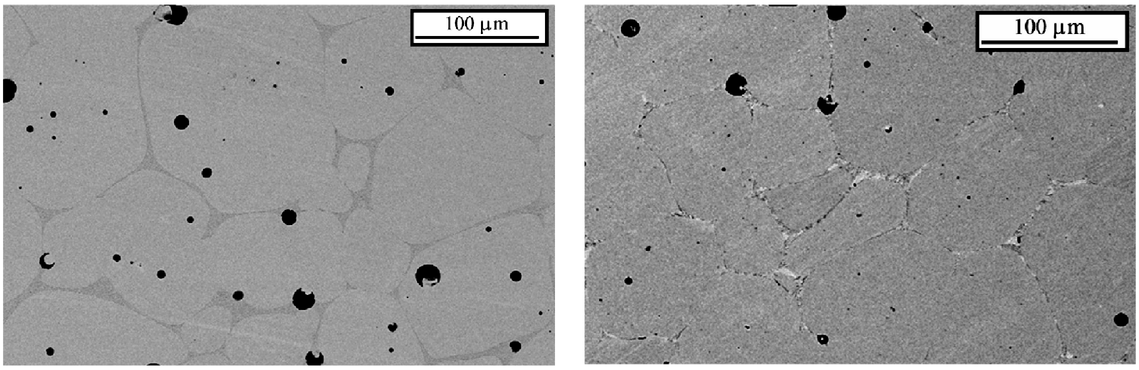

Figure 2.- SEM images of as-sintered microstructures of stainless steel (a) 304L and (b) 316L with 3%wt additions of CEITALOY HE.

After these events the final microstructure of these alloys is the typical one of a liquid phase sintered material. These are shown in Fig.2 for the 304L and 316L grades after 1 hr at 1280ºC to reach densities of 7.76 and 7.83 g/cm^3, respectively. It is also important to remark that sintering at temperatures between 1240 and 1280ºC gives as a result materials with apparent hardness values between 63 and 87 HRB thus exhibiting sizing capabilities.

Table 2.- Tensile properties and density of as-sintered powder compacts containing 3%wt additions of CEITALOY HE or CEITALOY HD.

Material designation	Sintering temperature (ºC)	Density (g/cm^3)	E%	UTS (MPa)
304L +3% HE	1280	7.76	64.28	914
316L +3% HE	1240	7.61	34.50	669
316L +3% HE	1280	7.83	37.70	776
316L +3% HD	1240	7.51	33.13	658
316L +3% HD	1280	7.69	38.92	665

One of the most important effects obtained with the use of these master alloys is the spherodisation of oxides that lead to the development of extremely clean, oxide free sintering necks. As a result of the formation of those strong metal-metal contacts an important improvement in properties was produced (Table 2). Images of the fracture surfaces observed under the SEM for these materials in the as-sintered state are shown in Fig. 3. These are noticeably ductile fractures which also allow clear identification of the spherodised oxides located inside the dimples. It should also be mentioned that after potentiodynamic tests the corrosion resistance of these alloys is superior to that of those PM alloys without master alloy additions.

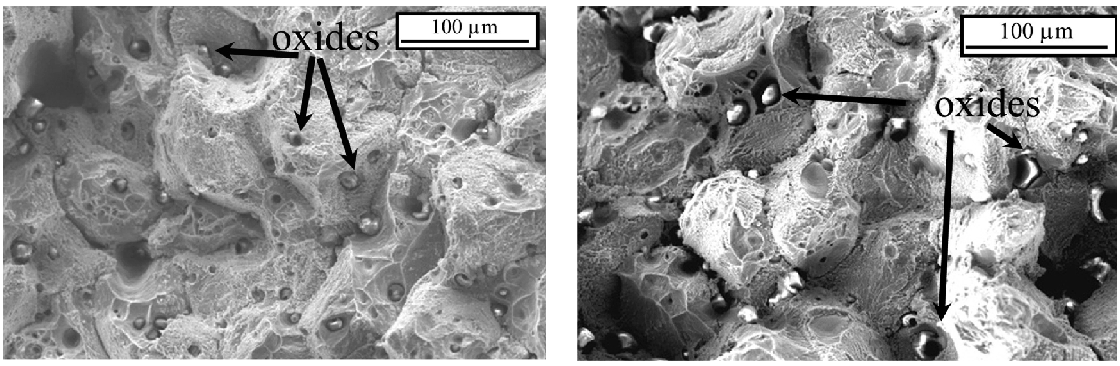

Figure 3.- Fracture surfaces of as sintered stainless steel (a) 304L and (b) 316L with 3%wt additions of CEITALOY HE after tensile testing.

Conclusions

The master alloys used as additions to the powder mixtures allow reaching full or near full density after liquid phase sintering of 316L and 314L austenitic stainless steels. As a result of the formation of strong metal-metal sintering necks and high density, encouraged by the use of these master alloys, the as sintered stainless steels develop outstanding tensile properties (in particular high ductility), and improved corrosion resistance.

Acknowledgements

The authors acknowledge the financial support to this work from SPRI of the "Departamento de Industria, Comercio y Turismo" of the Basque Government.

References

[1] M. C. Baran, A. E. Segall, B. A. Shaw, H. M. Kopech, T. E. Haberberger, Procs. of Adv. in Powder Met. and Particulate Materials, Chicago IL 1997, 37-42.
[2] E. Klar, P. K. Samal, *Powder Metal Technologies and applications, (ASM Handbook)* **6**, 476 (1998).
[3] C. M. Sonsino, R. Zieschang, V. Arnhold, H-H. Sandritter, D. Gonia, Procs. of PM World Congress, Granada 1998, 319-324.
[4] R. M. German, *Metallurgical Transactions A* **7**, 1879 (1976).
[5] H. S. Nayar, B. Wasiczko, *Metal Powder Report* **45**, 611 (1990).
[6] K. T. Kim, Y. C. Jeon, *Materials Science and Engineering A* **245**, 64 (1998).
[7] J. M. Capus, *Advanced Materials and Processes* **158**, 57 (2000).
[8] P. K. Samal, *Key Engineering Materials* **189-191**, 328 (2001).
[9] R. M. German, K. A. D'Angelo, *Int. Met. Rev.* **29**, 249 (1984).
[10] P. E. Zovas, R. M. German, K. S. Hwang, C. J. Li, *J. of Metals*, 28 (1983).
[11] M. Sarasola, T. Gómez-Acebo, F. Castro, *Powder Met.,* **48**, 59 (2005).
[12] K. Koichu, N. Mitsuru, H. Hiroshi, *Funtai Oyobi Fummatsu Yakin/J. of the Jpn. Soc. of Powder and Powder Met.* **47**, 1091 (2000).
[13] K. S. Narasimhan, *Materials Chemistry and Physics* **67**, 56 (2001).
[14] D. S. Madan, *The Int. J. of Powder Met.* **27**, 339 (1991).
[15] P.E. Busy, M. E. Warga, C. Wells, *J. of Metals Trans. AIME* **Nov.**, 1463 (1953).
[16] B. Hallemans, P. Wollants, J. R. Roos, *Z. Metallkunde* **85 (10)**, 676 (1994).
[17] S. K. Jensen, E. Maahn, Procs. of World Cong. on PM, Paris 1994, 2113-2116.
[18] A. Molinari, G. Straffelini, T. Pieczonka, J. Kazior, *Int. J. of Powder Met.* **34**, 21 (1998).
[19] A. Molinari, J. Kazior, F. Marchetti, R. Canteri, I. Cristofolini, A. Tiziani, *Powder Met* **37**, 115 (1994).
[20] A. Molinari, J. Kazior, G. Straffelini, *Mater Charact* **34**, 271 (1995).
[21] A. Molinari, T. Marcu Puscas, G. Straffelini, Procs. of Metallurgia Italiana 2001.
[22] P. K. Samal, J. B. Terrel, Procs. of Int. Conf. on Powder Met. & Particulate Materials, New York 2000, 17-31.
[23] T. Pieczonka, J. Kazior, A. Tiziani, A. Molinari, *J. of Mats. Proc. Technol.* **64**, 327 (1997).
[24] R. Bollina, R. M. German, Procs. of Euro PM2004, Vienna 2004, 335-342.
[25] C. Schade, J. Schaberl, S. N. Thakur, V. C. Dongre, Procs. of Int. Conf. on Powder Met. & Particulate Mats., Montreal 2005.
[26] C. T. Schade, J. Schaberl, Procs. of Euro PM2004, Vienna 2004, 116-123.
[27] R. M. German, *The Int. J. of Powder Met and Powder Technol.* **19**, 277 (1983).
[28] R. Tardon, R. M. German, *Int J Powder Metall* **34**, 40 (1998).
[29] M. Sarasola, S. Sainz, F. Castro, Procs. of Euro PM2005, Prague 2005, 349-356.