TRIBOLOGICAL PROPERTIES OF SINTERED AUSTENITIC Atrito Desgaste **STAINLESS STEELS**

Lubrificação

V.04

Effects of boron, yttria, and other additives

Mogueca Tribológica

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Programa de Pós-Graduação em Engenharia e Ciência dos Materiais



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Profa. María Cristina Moré Farias

- * Graduação Eng. Mecânica ISPJAE Cuba
- * Mestrado Eng. Mecânica USP
- * Doutorado Eng. Mecânica USP
- * Pós-Doutorado Eng. Mecânica USP
- Docente PPGMAT/UCS (2010 atual)

Principais Pesquisas

- Desenvolvimento e caracterização tribológica materiais sinterizados (metais, cerâmicas) com diferentes aditivos (ativadores, reforços, lubrificantes sólidos)
- Tribologia de materiais de fricção utilizados em freios automotivos

✤ Determinação de propriedades mecânicas de superfícies empregando indentação instrumentada

 Desenvolvimento de pavimentos cerâmicos base argila com adição de resíduos de rochas





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Professores PPGMAT 2019

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Corpo discente 2019: 17 alunos de mestrado e 26 de doutorado, além de estudantes de graduação realizando trabalhos de iniciação científica.

> Corpo docente permanente: 75% têm bolsa CNPq de Produtividade em Pesquisa, que distingue os pesquisadores com alta produtividade.

- 129 mestres formados.
- 24 doutores formados.
 - 45 patentes.

• 570 artigos.

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PPGMAT - UCS LINHA DO TEMPO





• Prof. Israel J. R. Baumvol é convidado a criar um Programa de Pós-Graduação em Materiais

2004 • Início das atividades do PPGMAT com 85 inscritos para 15 vagas

2005 • Primeira defesa de Mestrado, pela tecnóloga em Polímeros Maira Finkler

2006 · Convênio UCS-SIMECS para complementar recursos públicos para laboratório do PPGMAT

Inauguração do Laboratório de Engenharia de Superfícies e Tratamentos
 Térmicos (LESTT)

Início do Doutorado Interinstitucional PGCIMAT/UFRGS - PPGMAT/UCS
 Inauguração do Laboratório de Caracterização de Materiais I

2008 : O PPGMAT compõe a recém criada "Área de Materiais" da CAPES Inauguração do Núcleo de Pesquisas em Geoquímica (NupGeo)

- Criação do Instituto Nacional de Engenharia de Superfícies (INES)
- Convênio UCS-CIC para complementar recursos públicos ao laboratório do INES

 Início das atividades do Laboratório de Pesquisa em Química dos Materiais (LPQM)

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Sintered austenitic stainless steels





- Stainless steels have been successfully fabricated through different powder metallurgy (P/M) routes
- Austenitic (ASS) and ferritic (FSS) stainless steels are the most widely produced by P/M
- ASS exhibit a good combination of corrosion and oxidation resistance, associated with good mechanical properties
- Interest in P/M SS for general use (biomedical, dental, chemical, nuclear, automotive, aerospace) has increased



Sintered austenitic stainless steels

- P/M ASS present lower mechanical resistance than the wrought or cast steels, due to their intrinsic porosity
- Applications of ASS are also limited by their relative softness and susceptibility to wear (adhesive, abrasive, fatigue) and wear-corrosion
- Three routes have been implemented to improve density and reach a good combination of mechanical, wear and corrosion properties of P/M SS
 - i. surface modification of the sintered body by plasma-assisted surface treatments
 - ii. modification of parameters in compaction and sintering steps
 - iii. addition of certain elements (sintering enhancers or activators and reinforcements)





Activated sintering

- Activated sintering refers to any special process which results in an increased sintering rate or densification rate, i.e.,
 - promotes lowering sintering temperature; shorten sintering time or improve sintered properties

• Sintering enhancement approaches

- Solid state activated sintering
- Liquid phase sintering
- Sintering activators
 - small particles, frequently used in low concentrations
 - promote effective changes in interfacial energy, grain boundary mobility, reduction of void fraction, diffusion rates, and phase stability

R. M. German & B. H. Rabin (1985) Powder Metallurgy, 28:1, 7-12.





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Possible routes to alter sintering rate

- Change process conditions (particle size or temperature)
- Change defects configuration by pretreating powders (alloying or deformation)
- Application of external force (Ex. HP, HIP)
- Promote the formation of second phases that act as preferential diffusion paths
 - Solid state activated sintering
 - Liquid phase sintering

R. M. German & B. H. Rabin (1985) Powder Metallurgy, 28:1, 7-12.





Liquid phase sintering

- In the case of liquid-phase sintering, densification is achieved through the formation of a system with high wettability between the matrix and the liquid phase
 - improves the mass transfer rate
 - Increase the sintering rate by decreasing sintering temperature or reducing sintering time
- Liquid phase can be obtained by
 - addition of low melting temperature elements

□ Cu, P, Si, Cu-10Sn, Tin, Babbitt

dissociation of a mixture containing the base material and additive powders in a new phase with eutectic composition

□ B, Cr₂B, FeB, Fe₂B

R. M. German & K. A. D'Angelo (1984), International Metals Reviews, 29:1, 249-272.





Solubility: S_B/S_A > 1

- Favorable effect in diffusion rate
 - diffusive flux in additive layer
 - favorable change in bonding free energy
 - good wetting and adhesion of additive to base material



Idealized phase diagram showing characteristics most favorable for enhanced sintering

R. M. German & K. A. D'Angelo (1984), International Metals Reviews, 29:1, 249-272.







Segregation: T_{mB}/T_{LP} > 1

- Segregation of an equilibrium second phase at interparticle site
 - decreasing Decreasing liquidus and liquidus and solidus as A is solidus increased large melting examples: L+β point difference liquid phase activated α $\alpha + \beta$ low solubility high solubility additive base

R. M. German & B. H. Rabin (1985) Powder Metallurgy, 28:1, 7-12.



Diffusion: D_E/D_B > 1

- D_E: diffusivity of B in A layer
- D_B: selfdiffusivity of B
- additive flows to the interparticle boundary
- rapid diffusion along the sinter bond
- Iow liquid temperature for A
 - Iow activation energy
 - high diffusivity



R. M. German & B. H. Rabin (1985) Powder Metallurgy, 28:1, 7-12.







Sintering additives for ferrous powders

- Sintering activators
 - C, B, P,
 - Cu, Sn, S, Ni, Mn, Co, Ti
- Other additives
 - Al₂O₃, Y₂O₃
 - B₂Cr, Cr₂Al, TiCr₂, TiAl
 - VC, SiC, TiC
 - TiB₂

R. M. German & K. A. D'Angelo (1984), International Metals Reviews, 29:1, 249-272. Oke, S.R., Ige, O.O., Falodun, O.E. et al. (2019) Int J Adv Manuf Technol, 102, 3271–3290.





Other sintering additives

- In combination with solid state or liquid phase sintering activators, other elements have been added to
 - enhance mechanical properties
 - improve corrosion and high-temperature oxidation resistance
 - reduce friction and wear
- Low matrix-additive interaction makes necessary the use sintering activators
 - Solid lubricants (h-BN, MoS₂)
 - Reinforcement
 - □ Oxide ceramics (Al₂O₃, Y₂O₃) → mechanical properties, wear and corrosion resistance
 - □ Intermetallics (Cr_2Al , Ti Cr_2 , TiAl) → mechanical, corrosion and wear properties
 - \square Carbides (VC, SiC, TiC) \rightarrow mechanical properties, wear resistance
 - □ Borides (TiB₂) → mechanical and tribological properties
- The improvement of mechanical, corrosion and tribological properties of the composites depends on the amount, size, shape and distribution of the dispersed second phase particles, and P/M parameters

Oke, S.R., Ige, O.O., Falodun, O.E. et al. (2019) Int J Adv Manuf Technol, 102, 3271-3290.





Tribology properties of sintered austenitic stainless steels

- The literature on the tribological properties of P/M austenitic stainless steels and theirs composites is scarce
- There exist some researches on dry sliding behavior of sintered austenitic stainless steels added with
 - Metals or metallic alloys: B, Cu-Sn
 - Borides: TiB₂
 - Nitrides: BN
 - Oxides: Al₂O₃, Y₂O₃, YAG
 - Carbides: SiC, VC
 - Intermetallics: TiCr₂, Cr₂Al, Ni₃Al, Fe₃Al





Metal matrix composites (MMC)





Ref: German et al Review: liquid phase sintering. J Mater Sci (2009) 44:1–39

Powder metallurgy Secondary particle additives **Final Properties** Effect of sintering parameters as Sintering mechanism temperature on the sintered phase Higher hardness and density transformation **Oxidation resistance** Liquid phase sintering Importance of the particles: size, shape • Solid phase sintering Wear resistance and volume fraction Effect of mixture of different materials





Sintered Austenitic Stainless Steel

Precedents

- D. Uzunsoy, Investigation of dry sliding wear properties of boron doped powder metallurgy 316L stainless steel, Mater. Des. 31 (8) (2010) 3896–3900.
- M. Vardavoulias, M. Jeandin, F. Velasco, J.M. Torralba, Dry sliding wear mechanism for P/M austenitic stainless steels and their composites containing Al₂O₃ and Y₂O₃ particles, **Tribol. Int.** 29 (6) (1996) 499–506.
- A. Bautista, F. Velasco, J. Abenojar, *Oxidation resistance of sintered stainless steels: effect of yttria additions*, *Corros. Sci.* 45 (2003) 1343–1354.





Dry sliding wear of boron doped P/M ASS (Uzunsoy, 2010)





- Boron additions decrease plastic deformation and wear rate in sliding contact
- Hardness and porosity level have a significant effect on the wear behavior of P/M ASS





Sliding wear mechanism for P/M ASS and their composites (Vardavoulias et al., 1996)

Specimen	Friction coefficient	Disc specific wear rate (×10 ⁻¹³ m ² N ⁻¹)
304L	0.61	7
$304L+B_2Cr+Y_2O_3$	0.62-0.65	5.7
304L+B2Cr+Al2O3	0.8	2.1
304L+BN+Y ₂ O ₃	0.65-0.68	9.4
304L+BN+Al ₂ O ₃	0.6-0.7	6.1
316L	0.58	6.1
316L+B2Cr+Y2O	0.6-0.65	3.5
$316L + B_2Cr + A\overline{I}_2O_3$	0.6-0.65	3.4
$316L+BN+Y_2O_3$	0.62-0.65	4.7
$316L+BN+A\overline{l}_2O_3$	0.62-0.65	4.8

- Ceramic particles (Al₂0₃ and Y₂0₃) and sintering activators (B₂Cr, BN) improved wear resistance
- Ceramic particles limited plastic deformation while sintering activators decreased porosity
- □ Friction coefficient did not vary substantially (0.6 and 0.7)
- "Friction-induced martensite" (debris)





Oxidation resistance of sintered stainless steels (Bautista et al., 2003)



Sintered stainless steels	$k ({ m g}^2{ m cm}^{-4}{ m s}^{-1})$			
	600 °C	800 °C		
316L	-	1.4E-10		
304L	2.4E–11	8.1E-11		
304L + Yttria	2.4E–11	3.6E-10		
434L	4.0E–12	2.5E-12		





Sintered Austenitic Stainless Steel – recent results

- Friction and wear
- High-temperature oxidation

Effect of boron and yttria additions

<u>Team</u>

Profa. M. Cristina Moré Farias

Postgraduate students Collaborators professors





- Serafini, F.L., Peruzzo, M., Krindges, I., Ordoñez, M.F.C., Rodrigues, D., Souza, R.M., Farias, M.C.M. (2019) *Materials Characterization*, 152, pp. 253-264.
- Peruzzo, M., Serafini, F.L., Ordoñez, M.F.C., Souza,
 R.M., Farias, M.C.M. (2019) *Wear*, 422-423, pp. 108-118.
- Peruzzo, M., Beux, T.D., Ordoñez, M.F.C., Souza, R.M., Farias, M.C.M. (2017) *Corrosion Science*, 129, pp. 26-37.
- Serafini, F. L. ; Peruzzo, M. ; Beux, T. D. ; Ordoñez, M.F.C. ; Dotta, A. L. B. ; Souza, R.M. ; Farias, M.C.M. In: 6th World Tribology Congress, WTC2017, Beijing. 6th World Tribology Congress, WTC2017, 2017.

Further studies for P/M ASSs and their composites

- Friction and wear at high-temperature
- Tribocorrosion behavior

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P/M processing of ASS 316L



BRATS - Sintered Filters Special Metallic Powders (Cajamar, Sao Paulo, Brazil)



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Initial characterization of the sintered ASS 316L samples







Tribological characterization of the sintered ASS 316L samples





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Thermal analysis





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Microstructure





Microstructure of the B-free and B-containing sintered samples

- * Porosity
- Austenitic grains
- Phases at the grain boundaries

Peruzzo et al. (2019) Wear, 422-423, pp. 108-118.







Porosity analysis



Sample	Porosity (%)	Pore size, D ₉₀ (μm)	Circularity index, C _I		
316L	12.89	14.51	0.4		
316L-06B	5.66	20.51	0.8		
316-08B	7.7	26.17	0.8		

- Irregular and interconnected pores were formed for the boron-free sample
- Nearly circular and isolated pores were developed in the boron-containing samples

Serafini, F.L. et al. (2019) Materials Characterization, 152, pp. 253-264.





Microstructure



Serafini, F.L. et al. (2019) Materials Characterization, 152, pp. 253-264.



Microstructure – EDS mapping



Serafini, F.L. et al. (2019) Materials Characterization, 152, pp. 253-264.





Microstructure – EDS line

Serafini, F.L. et al. (2019) Materials Characterization, 152, pp. 253-264.



Line 1 – Continuous dark-grey phase, Cr-rich boride

Orthorhombic, Fe_{1.1}Cr_{0.9}B_{0.9}

Line 2 – Continuous light-gray phase, Cr- and Mo-rich boride

Cubic, Cr₂₃(B_{1.5}C_{4.5})

Line 3 – Discontinuous phase, Mo-rich boride

Tetragonal, Cr_{1.75}Mo_{0.25}B



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Crystalline phases

Sample	γ-Fe	M ₂₃ C ₆	M ₂₃ (B,C) ₆	Fe _{1.1} Cr _{0.9} B _{0.9}	Cr _{1.75} Mo _{0.25} B
	Cubic	Cubic	Cubic	Orthorhombic	Tetragonal
316L	95.47%	4.53%			
316L-0.6B	78.27%		6.39%	9.40%	5.94%
316L-0.8B	66.21%		15.46%	9.40%	7.91%



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Density and hardness

	Donaitu		Instrumented indentation hardness (GPa)				
Sample	(g/cm ³)	(HV ₁₀)	Austenite	Dark-grey boride, Cr-rich	Discontinuous boride, Mo-rich		
316L	7.13 ± 0.04	89 ± 3	1.6 ± 0.1	-	-		
316L-06B	7.37 ± 0.01	159 ± 13	1.9 ± 0.1	20.5 ± 1.3	4.3 ± 0.7		
316L-08B	7.35 ± 0.01	174 ± 7	1.9 ± 0.1	22.9 ± 2.1	5.0 ± 0.8		

Boron increases the hardness austenitic matrix and creates a network of hard borides along the austenitic grain boundaries

Serafini, F.L. et al. (2019) Materials Characterization, 152, pp. 253-264.







Reciprocating sliding wear



Boron addition

- Narrower and shallower wear tracks
- Improved wear resistance (less material removal) that can be related to
 - Rounded pores (stress concentration regions)
 - Hard borides (less plastic deformation)

Peruzzo et al. (2019) Wear, 422-423, pp. 108-118.







Friction behavior



Peruzzo et al. (2019) Wear, 422-423, pp. 108-118.



Worn surfaces

316L



316L-08B



Adhesive wear plastic deformation, material transferring and abrasion grooves

Peruzzo et al. (2019) Wear, 422-423, pp. 108-118.



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Worn surfaces



Peruzzo et al. (2019) Wear, 422-423, pp. 108-118.

Adhesive wear

- plastic deformation,
- material transferring and abrasion grooves

Oxidative wear by metallic

particle oxidation

transfer layer is a mixture of oxide and metallic particles) and composed of small clustered particles

I. Hutchings, P. Shipway, Tribology: Friction and Wear of Engineering Materials, 2017. F.H. Stott, Tribol. Int. 31 (1–3) (1998) 61–71.





Wear particles



Wear particles

plate and lamellar morphologies

same composition of transfer layer

Peruzzo et al. (2019) Wear, 422-423, pp. 108-118.





Single-pass sliding test

316L-06B

(e)

316L



Single-pass sliding test

Evaluation of load carrying capability of each microstructural constituent (austenite matrix and boron-based precipitates)

Restrict the formation of wear particles, plastic deformation, straininduced martensitic transformation or oxidation of surface

- Plastic deformation and abrasion grooves in the austenite matrix
- Borides are free of any damage

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Single-pass sliding test

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Material	E (GPa)	ν^{b}	H (GPa) ^a	W_E/W_T^a	E^*/H	σ/β^{c}	ψ	
Austenite matrix	195.30 ± 12.60 ^a	0.30	1.92 ± 0.08	0.15	82.59	2×10^{-4}	1.18	"Plastic contact" ψ > 0.6
Cr-rich boride	443.62 ± 18.74 ^a	0.20	20.52 ± 1.27	0.39	13.21	2×10^{-4}	0.18	"Elastic contact" ψ < 0.6
					1			ł

Plasticity index

 $\psi = \left(\frac{E^*}{H}\right) \left(\frac{\sigma}{\beta}\right)^{1/2}$

Energy ratio

$$rac{W_E}{W_T} = \lambda rac{H}{E^*}$$

Material	Dynamic hardness (MPa)	Friction coefficient
316L	510	0.22
316L-06B	1244	0.10

Borides have also load carrying capacity

J.A. Greenwood, J.B.P. Williamson, Proc. R. Soc. A: Math. Phys. Eng. Sci. 295 (1442) (1966) 300-319.







High-temperature cyclic oxidation at 900°C



- Boron to the 316L steel strongly improves the cyclic oxidation resistance
- Rounded and smaller pores contribute with the reduction in the porosity and the active area for oxidation, (this tendency is more pronounced in the boron-containing steel
- Yttria addition also improves the oxidation resistance of the steel in a lower ratio than boron

Peruzzo, M., et al. (2017) Corrosion Science, 129, pp. 26-37.





ASS obtained by SPS – recent results





Serafini, F.L. et al. (to be published).



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ASS obtained by SPS – recent results



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	Base material	Additive type	Additive amount (wt%)	Density (g/cm³)	Hardness	k mm³/Nm	Sintering parameters
[1]	6.90 g/cm ³ 110 HV5	Y ₂ O ₃	1 – 5	6.95 – 6.92	127 – 155	•••	1300 °C, 1 h, Hydrogen
[2]	6.90 g/cm ³ 110 HV5	Y_2O_3 Cu Cu-Sn Fe ₃ P Si	3 1-3 1-2 1-5	•••	122 104 - 100 135 - 127 171 - 218 85 - 80	•••	1300 °C, 1 h, Hydrogen
[3]	6.90 g/cm ³ 38 HRB 6.1x 10 ⁻¹³ mm ³ /Nm	$Y_2O_3-B_2Cr$ Y_2O_3-BN	5-2 5-1	7.35 7.05	74 63	3.5x 10 ⁻¹³ 4.7x 10 ⁻¹³	1250 °C, 30 min, Vacuum
[4]	6.5 g/cm ³	Y ₂ O ₃	10	6.18	•••	•••	1250 °C, 60 min, Hydrogen
[5]	6.61 g/cm ³ 82 HV5	Y ₂ O ₃	3 – 8	6.35 - 6.08	118 – 125	•••	1350 °C, 1 h, Hydrogen

[1] S. Lal, G.S. Upadhyaya. J. Mater. Sci. 24 (9) (1989) 3069–3075.

[2] S. Lal, G.S. Upadhyaya. Sol. Sta. Phen. 8-9 (1990) 361–368.

[3] M. Vardavoulias, et al. Tribol. Int. 29 (6) (1996) 499–506.

[4] J. Shankar, et al. Corros. Sci. 46 (2004) 487–498.

[5] A. Raja Annamalai et al. Corros. Eng. Sci. Technol. 50 (2015) 91–102.

Data compilation Properties of P/M ASS





Data compilation

Effect of additives in density of P/M ASS



Sintered Austenitic Stainless Steel





Final remarks

- Boron can be used either elemental or in compound (FeB, Fe₂B, NiB and Cr₂B) as an additive in ironbased systems and stainless steels
- Boron acts as a sintering enhancer, and sintering temperature can be reduced to about 1240 °C
- The addition of boron in elemental form results in the good properties and structure for stainless steel
- Boron addition up to 0.8 wt% for 316L stainless steel powders increases density, mechanical properties, corrosion, and wear resistance. Nearly full densification was obtained with enough eutectic phase formation
- Yttria addition improves high-temperature oxidation of P/M ASS.
- The resultant parts might be used in applications where wear and high-temperature resistance are desired



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