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Size matters: Mechanism of metal release from 316L stainless steel particles is governed by size-dependent properties of the surface oxide

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ABSTRACT

Size-dependent health aspects due to exposure to micro- or nano-sized particles can only be fully understood if their physicochemical properties are well characterized. The aim of this study was to explain the process of metal release from well-characterized inert gas atomized stainless steel 316L particles, sized <4 μm (fine) and <45 μm (coarse), in aggressive environments of relevance for inhalation and cellular uptake. This was accomplished by correlating new results from real-time metal release measurements with particle- and surface oxide characteristics. In simulated biological media with complexing properties, a complexation (ligand)-induced dissolution mechanism is dominating the metal release from fine 316L particles (having a homogeneous and amorphous Mn-rich surface oxide due to rapid cooling). At similar conditions, the coarse 316L particles show a metal release mechanism dominated by fast dissolution of surface oxide nanoparticles (rich in Mn, Fe, and some S), acting as initiation sites for metastable pitting corrosion.

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1. Introduction

Health aspects related to human exposure to metal-containing micro- or nano-sized particles can only be fully understood if their physicochemical properties are well characterized [1]. It has been demonstrated that particles of different sizes have different toxic and surface oxide properties [2]. The aim of this study was to explain the metal release process of well-characterized micro-sized stainless steel 316L particles in aggressive environments of relevance for inhalation and cellular uptake. Metal release may in certain conditions of this study result from chemical or electrochemical dissolution of the surface oxide and/or from corrosion of the bulk metal.

2. Material and methods

Inert gas atomized stainless steel grade AISI 316L particles, sized <4 μm, denoted "fine", and <45 μm, denoted "coarse" were used in this study. Their specific surface areas are 0.700 (fine) and 0.069 (coarse) m^2/g. The particles were thoroughly characterized in previous studies [3–8]. Key information is visualized and presented in Fig. 1.

Time-resolved metal release measurements were performed using a modified inductively coupled plasma optical emission spectroscopy instrument (ICP-OES) from HORIBA JobinYvonUltima 2C™ [9]. The particles (0.1 g) were placed in a special built flow cell consisting of a Teflon cylinder (1 mL volume) enclosed with membrane filters (sterile PALL Acrodisc® 0.2 μm Supor membrane) on each side to avoid particle loss. The solution was passed through the cell volume (2.0–2.2 mL/min) without particles inside (blank measurements and calibration) and with particles loaded (sample measurements) during 30 min.

Two solutions, artificial gastric fluid (GST, pH 1.5) and artificial lysosomal fluid (ALF, pH 4.5) were used for measurements (GST: 4 g/L 25% HCl. ALF: 20.8 g/L $C_6H_8O_7$, 6.00 g/L NaOH, 3.21 g/L NaCl, 0.050 g/L $MgCl_2$, 0.071 g/L Na_2HPO_4, 0.039 g/L Na_2SO_4, 0.128 g/L $CaCl_2 \cdot 2H_2O$, 0.077 g/L $C_6H_5Na_3O_7 \cdot 2H_2O$, 0.059 g/L H_2NCH_2COOH, 0.090 g/L $C_4H_4O_6Na_2 \cdot 2H_2O$, 0.085 g/L $C_3H_5NaO_3$, 0.086 g/L $C_3H_3O_3Na$, and 1.7 mL/L 50% NaOH). They were chosen as rather aggressive solutions

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Oxide wt %	"Fine" < 4 μm	"Coarse" < 45 μm
Fe(II)*/Fe(III)	40	72
Cr(III)	14	15
Mn(II)*/Mn(III)*/Mn(IV)*	47	13

* ?

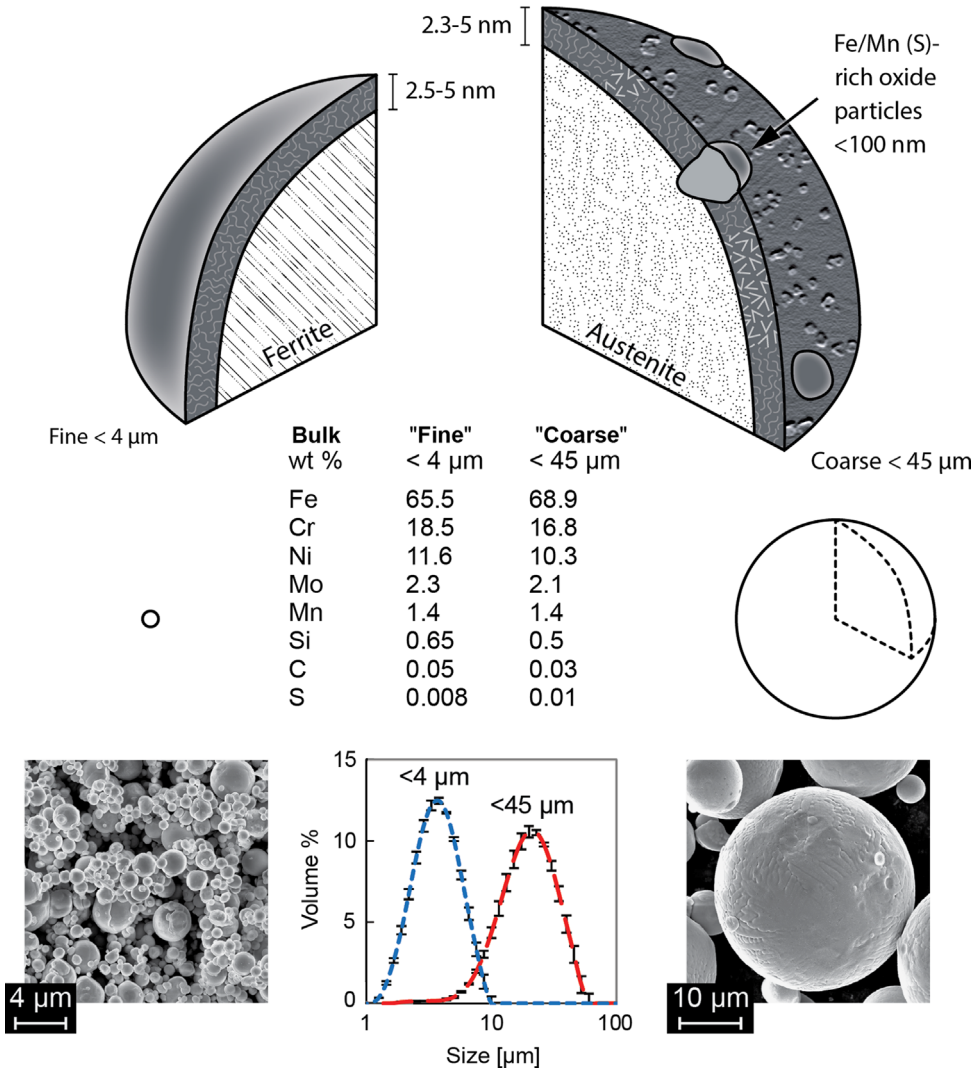


Fig. 1. Compilation of bulk and surface characteristics of fine (left) and coarse (right) 316L particles: crystallographic structure [5], oxide speciation [7,8], scanning electron microscopy images, and particle size distribution in phosphate buffered saline [6].

simulating acidic stomach conditions and intracellular fluid based on previous investigations [4,10]. The limits of detection were <2.9 (Fe), <7.0 (Cr), <8.7 (Ni), <6.2 (Mo), <0.5 (Mn), and <3.1 (Cu) μg/L, for both solutions tested.

3. Results and discussion

Fig. 2 shows real-time metal release from fine and coarse 316L particles in GST (pH 1.5) and ALF (pH 4.5).

Rapid cooling during inert gas atomization of the 316L particles strongly affects their bulk crystal structure [5] and surface oxide speciation (such as surface composition, phase, phase distribution, thickness, crystallinity, impurities) [7,8], cf. Fig. 1. The particles show significantly different magnetic properties, catalytic properties, surface oxide composition, corrosion properties (passivity) compared with massive sheets of the same nominal bulk composition [5,7,8].

The delayed increase of Fe release, observed for fine particles in the complexing solution ALF, Fig. 2, confirms previous postulations of a delayed complexation (ligand)-induced metal release mechanism in complexing solutions [4]. Interestingly, this is only seen for the fine particles, not for the coarse ones, Fig. 2. This fact suggests that the complexation-induced metal release is the dominating mechanism for the fine particles due to a highly homogenous and amorphous surface oxide [7,8], susceptible to ligand-induced dissolution [4] but resistant to pitting corrosion [8] as illustrated in Fig. 3. In contrast, the semi-crystalline surface oxide of the coarse particles is suggested to hinder ligand-induced dissolution [4,8]. Instead, Mn-, Fe- and sometimes S- rich surface oxide nanoparticles [7,8] are quickly dissolved and may act as pitting corrosion initiation sites [8,11]. This rapid dissolution of the surface oxide nanoparticles, resulting in metastable pitting, is

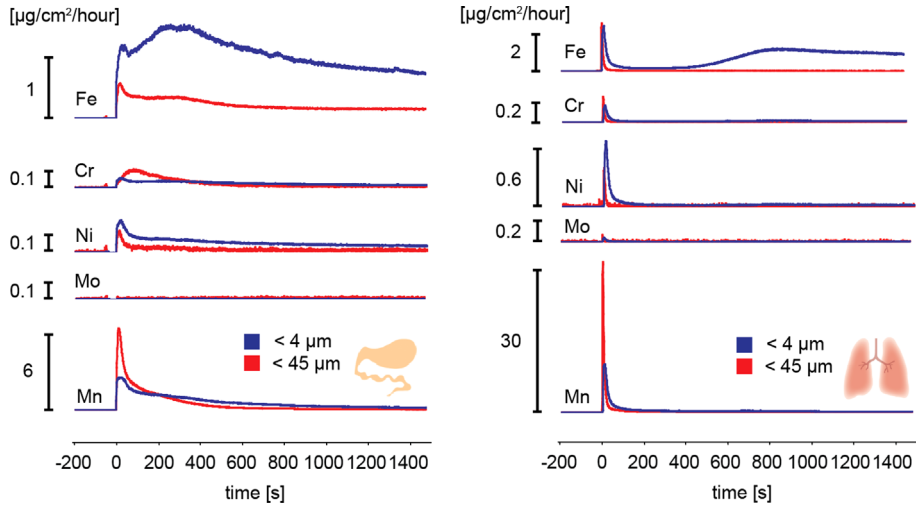


Fig. 2. Highly time-resolved metal release into GST (pH 1.5, left) and ALF (pH 4.5, right) from fine (blue) and coarse (red) 316L particles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

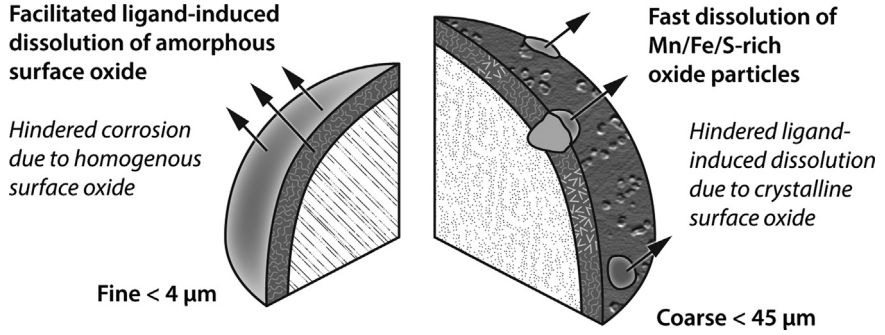


Fig. 3. Schematic illustration of the most dominant mechanisms of metal release for the fine (left) and coarse (right) 316L particles.

confirmed by results shown in Fig. 2 (Mn and Fe in ALF) and other results from previous time-resolved open circuit potential measurements [8].

The relatively high initial release of Ni for the fine 316L particles, Fig. 2, is most probably related to impurity particles of Ni–Cr particles, present in this size fraction [5,7,8].

The main reason for the higher levels of metal release generally occurring in ALF, Fig. 2, is the complexation capacity of citric acid, not the solution pH as was previously demonstrated [4,6].

A specific particle size, where one dominating mechanism of metal release changes to another, cannot be determined from results of this or previous studies. For particles smaller than ~10 µm in diameter, the bulk structure changes from an austenitic to a metastable ferritic phase due to more rapid cooling at manufacture [5]. From high-resolution SEM images [8], it can be deduced that oxide nanoparticles are present for particles larger than ~5 µm in diameter. This suggests that metal release from particles above this diameter is dominated by the dissolution of the Fe/Mn/S-rich oxide nanoparticles.

4. Conclusion

Highly time-resolved measurements of metal release suggest a dominating complexation (ligand)-induced dissolution mechanism for the rapidly cooled fine (< 4 µm) 316L particles (homogeneous and amorphous Mn-rich oxide). In contrast, the metal release mechanism for the coarse (< 45 µm) 316L particles is suggested to be dominated by fast dissolution of surface oxide nanoparticles (rich in Mn, Fe, and some S) that may act as initiation sites for metastable pitting corrosion.

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References

[1] Oberdörster G, Maynard A, Donaldson K, Castranova V, Fitzpatrick J, Ausman K, et al. Principles for characterizing the potential human health effects from exposure to nanomaterials: elements of a screening strategy. Part Fibre Toxicol 2005;2:8.
[2] Roduner E. Size matters: why nanomaterials are different. Chem Soc Rev 2006;35:583–92.
[3] Hedberg Y, Gustafsson J, Karlsson HL, Möller L, Odnevall Wallinder I. Bioaccessibility, bioavailability and toxicity of commercially relevant iron- and chromium-based particles: in vitro studies with an inhalation perspective. Part Fibre Toxicol 2010;7:23.
[4] Hedberg Y, Hedberg J, Liu Y, Odnevall Wallinder I. Complexation- and ligand-induced metal release from 316L particles: importance of particle size and crystallographic structure. BioMetals 2011;24:1099–114.
[5] Hedberg Y, Karlsson O, Szakalos P, Odnevall Wallinder I. Ultrafine 316L stainless steel particles with frozen-in magnetic structures characterized by means of electron backscattered diffraction. Mater Lett 2011;65:2089–92.

[6] Hedberg Y, Mazinanian N, Odnevall Wallinder I. Metal release from stainless steel powders and massive sheet - comparison and implication for risk assessment of alloys. Environ Sci Process Impacts 2013;15:381–92.
[7] Hedberg Y, Norell M, Hedberg J, Szakálos P, Linhardt P, Odnevall Wallinder I. Surface characterisation of fine inert gas and water atomised stainless steel 316L powders: formation of thermodynamically unstable surface oxide phases. Powder Metall 2013;56:158–63.
[8] Hedberg Y, Norell M, Linhardt P, Bergqvist H, Odnevall Wallinder I. Influence of surface oxide characteristics and speciation on corrosion, electrochemical properties and metal release of atomized 316L stainless steel powders. Int J Electrochem Sci 2012;7:11655–77.
[9] Ogle K, Baeyens J, Swiatowska J, Volovitch P. Atomic emission spectroelectrochemistry applied to dealloying phenomena: I. The formation and dissolution of residual copper films on stainless steel. Electrochim Acta 2009;54:5163–70.
[10] Midander K, de Frutos A, Hedberg Y, Darrie G, Odnevall Wallinder I. Bioaccessibility studies of ferro-chromium alloy particles for a simulated inhalation scenario: a comparative study with the pure metals and stainless steel. Integr Environ Assess Manag 2010;6:441–55.
[11] Hedberg Y, Virtanen S, Odnevall Wallinder I. Micro-capillary electrochemical and microscopic investigations of massive and individual micrometer-sized powder particles of stainless steel 316L. Int J Electrochem Sci 2012;7:11678–95.