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ScienceDirect
Journal of Food Engineering 87 (2008) 291–300
JOURNAL OF FOOD ENGINEERING
www.elsevier.com/locate/jfoodeng

Corrosion-induced release of chromium and iron from ferritic stainless steel grade AISI 430 in simulated food contact

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Received 28 August 2007; received in revised form 29 November 2007; accepted 1 December 2007
Available online 8 December 2007

Abstract

Ferritic stainless steel grade AISI 430 with three different surface finishes, glossy, line and abraded has been evaluated regarding changes in metal release rates and corresponding changes in surface composition when immersed in 3 vol% acetic acid at two different temperatures, 40 °C for ten days and 100 °C during three consecutive immersions of 30 min each. Test parameter intervals were set by one of the very few regulatory texts for metal release in food applications, the Italian law text D.M. 21-03-1973, Art. 37. The metal release process was found to be strongly dependent on surface area to solution volume ratio where a specific surface finish would be within the allowed limit, 0.1 mg Cr L^{-1} for the lowest ratio, 0.5 cm, but exceeded for the highest ratio, 2 cm^{-1}. The amount of released metal increased with increasing temperature and increasing surface roughness (surface finish).

Generated data show the regulatory text insufficient and to provide large degrees of freedom, specifically in terms of defining the surface area to solution volume ratio and the acidic cleaning of test vessels, essential parameters to enable reproducible and relevant migration data.

Keywords: Metal release; Acetic acid; Ferritic stainless steel; Iron; Chromium; Cuttlery

1. Introduction

Due to indisputably high corrosion resistance and beneficial mechanical properties compared with other materials, stainless steels are commonly used in food processing applications, in cooking utensils and in cutlery. The most frequently used grades within this context are the austenitic grades such as AISI 304 and AISI 316, both containing 8–10 wt% Ni (Council of Europe, 2001). Alloying with nickel enhances the corrosion resistance of the stainless steel grade, which generally has a retarding effect on the migration rate (metal release) (Herting et al., 2007a). However, nickel is relatively expensive on the market, and questioned from a toxicological point of view. Sufficient corrosion resistance can however be obtained without nickel as long as the chromium content is high enough (12 wt% Cr), and the area of application is not too corrosive. By using ferritic grades such as AISI 430 in e.g. kitchen utensils, potential adverse health effects due to nickel release are eliminated. However, the question of potential effects caused by chromium remains. Chromium is generally considered as an essential element for humans (Anderson, 1992; Cohen et al., 1993; Mertz, 1993). A daily intake of 50–200 μg chromium per day is recommended by the US national Council (Aitio, 1996) and the WHO limit for drinking water is set to 50 μg L^{-1} (World Health Organization, 2006). However, a too high dose of chromium may cause toxic effects. The dose of chromium intake that may cause toxic effects depends on many parameters including chemical state and the environment. Adverse health effects are generally not be expected from a daily intake of 10 mg/person (Expert group on Vitamins and Minerals, 2007). The toxicological endpoint, LD50, for rats have been determined to be 20–250 mg Cr(IV) and

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doi:10.1016/j.jfoodeng.2007.12.006

185–615 mg Cr(III) per kg body weight respectively (World Health Organization, 2003).

Some data exist in the scientific literature on the release of chromium from stainless steel in food contact (Offenbacher and Pi-Sunyer, 1983; Kuligowski and Halperin, 1992; Kumar et al., 1994; Flint and Packirisamy, 1997) but data is scarce for metal release into acetic acid.

All materials used for applications in direct or indirect contact with humans, such as food related items, may cause adverse health effects. Regulations, restrictions and protocols are hence often available to avoid the use of materials that exceeds stipulated limit values for e.g. metal migration (metal release). Different regulations exist on how to test stainless steels used for various food applications and stipulate maximum levels of metal release that do not cause adverse effects on human health (EN 1186-3, D.M. 21-03-1973). Acetic acid is recommended for testing of metal articles in contact with acetic foodstuffs (Food Standards Agency, 2003). However, no standardised test is adopted to determine released chromium from stainless steel in food contact.

One of the most detailed regulations is the Italian law text on global migration, D.M. 21-03-1973, Art. 37. The description of the test procedure in the law text is schematically illustrated in Fig. 1.

The aim of this study was to (i) evaluate the applicability of the Italian law text in its current form to determine metal release rates of chromium and iron from ferritic stainless steel grade AISI 430 when exposed to acetic acid, (ii) to elucidate the influence on kinetic effects of crucial experimental parameters including surface finish, surface composition, temperature and surface area to solution volume ratio on the released metal, and (iii) to provide scientific arguments for the need of improved regulatory protocols on global metal migration.

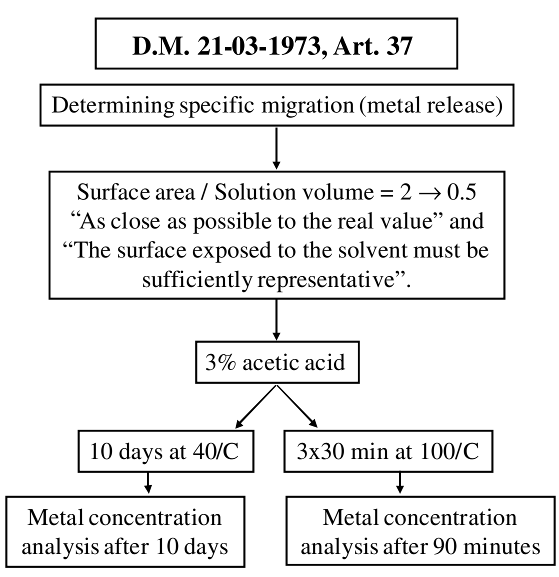

Fig. 1. Schematic illustration of general information on how to determine metal migration from metal articles in food contact, according to the Italian law text D.M. 21-03-1973, Art. 37.

2. Experimental

2.1. Material and sample preparation

Ferritic stainless steel grade 430, supplied by IKEA Sweden AB, was investigated in this study. The bulk composition of the steel is given in Table 1.

Differences in release rates were determined for various surface finishes; glossy, line, and abraded (1200 grit) with surface roughness (R_a) of 0.075 ± 0.006, 0.37 ± 0.04 and 0.23 ± 0.007 μm, respectively. Glossy and line surfaces were exposed in their as-received surface condition, representing two commonly used product surfaces. Abraded surfaces (wet ground to 1200 grit using silicon carbide paper for approximately 3 min) were primarily used to supply well-defined surfaces to be used for comparative purposes. Prior to exposure, the samples were ultrasonically cleaned in acetone and isopropyl alcohol, respectively, rinsed in isopropyl alcohol and dried with nitrogen gas. Ultrasonic cleaning was performed in each solvent during 6 min for the abraded surfaces, and during 3 min for the supplier made surface finishes.

Since only one side of the stainless steel grade was supplied with a specific surface finish, glossy or line, the surface without that specific surface finish was covered with a lacquer. Prior to any exposure, the lacquer was carefully tested for adequate adhesion to the stainless steel samples, and its capacity to act as a barrier for metal release from the stainless steel surface without potential release of metals from the lacquer in itself. The lacquer was tested by applying it to stainless steel samples and pure copper samples to determine that no iron or chromium was released through the lacquer, and subsequently running them through the entire immersion test and analysis as described below. The copper samples were used to determine that no iron or chromium was released from the lacquer itself. The lacquer was proven to have the desired properties.

2.2. Immersion test

Metal release studies (metal migration) were performed in accordance with the Italian law text D.M. 21-03-1973 (D.M. 21-03-1973, 1973). The law text suggests 3% acetic acid as a relevant solution to evaluate metal release from stainless steel used in food related applications after 10 days at 40 °C, and/or after three consecutive, 30 min long, immersions at 100 °C. The exposed surface area to solution volume ratio is recommended to anything between 0.5 and 2, unit is undefined.

The importance of temperature and surface area to solution volume ratio on the metal release process and its kinetic was determined for stainless steel grade 430 of

Table 1
Bulk composition of stainless steel grade 430 (wt%)

C	Cr	Ni	S	P	Si	Mn	N	Fe
0.045	16	0.1	0.002	0.034	0.28	0.46	0.05	Balanced