Study on the Influence of Metal Materials on the Migration of Heavy Metals in Stainless Steel Kitchenware

Yuan Chen1,*, Hehai Lin1, Jiaxin Chen1, Xufeng Zhou1, Liangsheng Zhou1, Weiguo Huang1, Quanyue Guan1, Guangbao Ye1

1Yangjiang Supervision Testing Institute of Quality & Metrology, Yangjiang, China;

*Corresponding author e-mail: 574527940@qq.com

Abstract. In this paper, the migration of heavy metal Ni and Cr was tested and compared for several kinds of food contact stainless steel materials 430, 304, 20Cr13, 30Cr13, 30Cr14, 50Cr15MoV and Germany 1.4116. Study the effect of different materials on the migration of heavy metals. The results show that the migration of austenitic stainless steel is significantly less than that of martensite. The migration of different materials is different. 50Cr15MoV and 30Cr13 are more likely to have migration than the national standard. The migration of 20Cr13 and 30Cr14 is relatively lower. Germany 1.4116 has the least amount of migration; the same material, the migration of the product is also very different, which has a greater impact on the microstructure of the material. The metallographic structure corresponding to the product with low heavy metal migration is uniform and dense, and the metallographic structure corresponding to the product with high heavy metal migration is coarser, and the density and uniformity are poor.

1. Introduction

Stainless steel kitchen utensils have entered the kitchen due to their anti-corrosion and easy-cleaning properties. However, the excessive migration of heavy metals has become an important issue for users in recent years. At the same time, it brings great pressure to Kitchenware companies. Stainless steel precipitates metal elements (such as Ni and Cr) due to its material contact with acidic food medium, which is absorbed by the body and accumulates, which is harmful to health. How to avoid and reduce the metal migration of stainless steel has become a major problem in the industry, and related testing institutions have also carried out a series of studies.

In China's mandatory standard GB 4809.9-2016 [1], the migration of Ni and Cr elements in stainless steel products are prescribed. The pretreatment process of food contact materials is specified in GB 5009.156-2016 [2] and GB 31604.1-2016 [3], and the instrumental analysis method for the migration of various heavy metal elements is specified in the national standard GB 31604.49-2016 [4]. The method specifies the use of a 4% concentration of acetic acid solution as a food simulant to simulate an acidic medium in contact with a stainless steel product.

This study selected several kinds of food utensils used in the market for stainless steel materials 430, 304, 20Cr13, 30Cr13, 30Cr14, 50Cr15MoV and Germany 1.4116[5]. According to the above national standard test method, 51 products were tested for migration of Ni and Cr elements. The influence of the material of the product on heavy metals migration was analyzed, and the mechanism analysis was carried out in combination with the microstructure of the product.
2. Experimental Section

2.1. Sample preparation
According to the different materials, according to the coverage of several materials commonly used in the market, select the appropriate sample quantity, and the sample preparation is shown in Table 1.

| Stainless steel grade | Stainless steel type | Product Category | Number of samples |
|-----------------------|----------------------|------------------|------------------|
| 430                   | Austenite           | Salad spoon, potato pressure, spoon, oil separator, soup spoon, shovel, fishing rod | 7                |
| 304                   | Austenite           | Food clips, forks, spoons | 4                |
| 20Cr13                | Martensite          | Burdock, chicken bone scissors, kitchen scissors, fruit knife | 5                |
| 30Cr13                | Martensite          | Fruit knives, kitchen scissors, kitchen knives, meal knives, tomato juice knives, slicing knives, fish knives, etc. | 20               |
| 30Cr14                | Martensite          | The burdock knife, the chef knife, the universal knife, etc. are mainly knife products. | 8                |
| 50Cr15MoV             | Martensite          | Meat cleaver, peel knife, universal knife | 4                |
| Germany 1.4116        | Martensite          | Fruit knife, peel knife | 3                |

2.2. Migration test
All samples were subjected to the immersion test of food contact materials according to the standard GB 5009.156-2016 [2] and GB 31604.1-2016 [3] to determine the immersion area and volume. After boiling for 30 minutes with 4% acetic acid, soak for 24 hours at room temperature, repeat the soaking three times. Take the third soaking solution for heavy metal migration test.

2.3. Determination of metal migration Ni and Cr in soaking liquid
The migration of heavy metal elements such as Ni and Cr was tested by inductively coupled plasma mass spectrometry (Agilent, ICPMS-7900, USA). The instrument conditions are listed in Table 2 and Table 3.

| Instrument parameters | Value | Instrument parameters | Value |
|-----------------------|-------|-----------------------|-------|
| RF power              | 1500W | Nebulizer             | Concentric nebulizer |
| Plasma gas flow       | 15 L/min | Sampling cone | Nickel cone |
| Carrier gas flow      | 1 L/min | Acquisition mode | Ski jump spectrum |
| Auxiliary gas flow    | 1 L/min | Collection points | 3 |
| Helium flow           | 5 mL/min | Detection method | automatic |
| Spray chamber temperature | 2 °C | repeat times | 3 |

| Element | Mass-to-charge ratio | Internal standard element | Analysis mode | Standard series |
|---------|----------------------|---------------------------|--------------|-----------------|
| Cr      | 52                   | Sc (45)                   | Collision mode | (5,10,50,100,200) ug/L |
| Ni      | 60                   | Ge (72)                   | Normal/collision mode | (5,10,50,100,200) ug/L |
2.4. Determination of chemical composition of stainless steel
The composition of the sample was measured by a fixed metal analysis spectrometer (Spike, Germany, floor-standing, MAXX). Test the same sample in three different parts and take the average.

2.5. Metallographic microstructure inspection
Metallographic microstructure analysis was carried out using an intelligent inverted metallographic microscopic image analysis system (German Card Microsystems, DMI 3000 M).

3. Results and discussion

3.1. Effect of composition and microstructure of stainless steel on migration
Three independent samples were selected for each material to test the composition and metal migration of the sample, and the effect of the morphology on the migration was compared.

| Sample number | Stainless steel grade | Chemical composition | Stainless steel type | Cr migration mg/kg | Ni migration mg/kg |
|---------------|-----------------------|----------------------|----------------------|-------------------|-------------------|
| S01           | 430                   | 0.04 16.40 0.149     | Austenite            | 0.02              | 0.003             |
| S02           | 430                   | 0.06 16.18 0.08      | Austenite            | 0.01              | 0.009             |
| S03           | 430                   | 0.07 16.04 0.115     | Austenite            | 0.008             | 0.02              |
| S04           | 304                   | 0.08 18.32 8.16      | Austenite            | 0.02              | 0.003             |
| S05           | 304                   | 0.07 18.26 8.07      | Austenite            | 0.03              | 0.008             |
| S06           | 304                   | 0.08 18.13 8.05      | Austenite            | 0.03              | 0.03              |
| S07           | 20Cr13                | 0.250 12.64 0.100    | Austenite            | 17.1              | 0.28              |
| S08           | 20Cr13                | 0.245 12.80 0.207    | Austenite            | 13.5              | 0.15              |
| S09           | 20Cr13                | 0.192 12.27 0.113    | Austenite            | 0.05              | 0.01              |
| S10           | 30Cr13                | 0.296 12.64 0.140    | Martensite           | 125.5             | 1.51              |
| S11           | 30Cr13                | 0.301 12.37 0.130    | Martensite           | 19.7              | 0.01              |
| S12           | 30Cr13                | 0.319 12.50 0.136    | Martensite           | 0.07              | 0.0005            |
| S13           | 30Cr14                | 0.324 13.43 0.119    | Martensite           | 42.2              | 0.5               |
| S14           | 30Cr14                | 0.390 13.43 0.152    | Martensite           | 8.7               | 0.11              |
| S15           | 30Cr14                | 0.384 14.10 0.143    | Martensite           | 1.09              | 0.02              |
| S16           | 50Cr15MoV             | 0.460 14.33 0.112    | 83.8                 | 1.8               |
| S17           | 50Cr15MoV             | 0.442 14.37 0.239    | 72.3                 | 2.2               |
| S18           | 50Cr15MoV             | 0.540 14.79 0.121    | 0.05                 | 0.009             |
| S19           | Germany1.4116         | 0.470 14.35 0.178    | 1.6                  | 0.03              |
| S20           | Germany1.4116         | 0.476 14.37 0.182    | 0.08                 | 0.003             |
| S21           | Germany1.4116         | 0.543 14.57 0.210    | 2.2                  | 0.04              |

The data in Table 4 shows that there is no linear correlation between the migration of stainless steel and its corresponding content of this element. The microstructure of stainless steel has a great influence on the migration amount, and the migration of austenitic stainless steel is significantly less than that of martensite. Comparing the content of carbon (C) and chromium (Cr) in stainless steel, the reason is that the martensite has a higher carbon content than austenite. In an acidic medium, the electrochemical reaction between carbon and other metal elements in the material is more intense, resulting in more obvious migration of metal elements [6]. The second reason is that chromium is the main element of corrosion resistance of stainless steel, austenite is 16-18%, martensite is 12-15%, austenite has higher chromium content than martensite[7], The migration is significantly lower.

3.2. Effect of different materials on the migration
The domestically produced materials with martensite stainless steel were selected for comparative test. Several materials were compared with 20Cr13, 30Cr13, 30Cr14, 50Cr15MoV and Germany
The heavy metal migration data of all the samples participating in the test were sorted and summarized. Since the German standard 1.4116 is equivalent to the national standard 50Cr15MoV, the data is classified into 50Cr15MoV.

### Table 5. Effect of different materials on the migration of metal elements

| Stainless steel grade | Number of samples | Cr migration mg/kg | Ni migration mg/kg | Excess quantity | Excess rate |
|-----------------------|-------------------|--------------------|-------------------|----------------|-------------|
| 20Cr13                | 5                 | 0.05-18.5          | 0.01-0.28         | 0              | 0           |
| 30Cr13                | 20                | 0.07-125.5         | 0.0005-1.5        | 3              | 15          |
| 30Cr14                | 8                 | 1.1-46.9           | 0.02-0.34         | 0              | 0           |
| 50Cr15MoV             | 7                 | 0.05-83.8          | 0.003-2.4         | 3              | 43          |

The data in Table 5 shows that the migration amount of different materials is quite different. Samples of the two materials, 30Cr13 and 50Cr15MoV, are more prone to migration than the national standard, and the migration of samples of 20Cr13 and 30Cr14 is relatively low. This may be due to the higher carbon content of 30Cr13 and 50Cr15MoV relative to 20Cr13 and 30Cr14, which makes the metal elements easier to migrate out.

### 3.3. Comparison of heavy metal migration between the same materials

For the samples of 10 stainless steels of 30Cr13 and 7 samples of 50Cr15MoV, the migration tests of the same materials were compared. The test results are listed in Table 6 and Table 7.

#### Table 6. Heavy metal migration data of 30Cr13 material samples

| Sample number | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 |
|---------------|----|----|----|----|----|----|----|----|----|-----|
| Cr (mg/kg)    | 100.9 | 56.4 | 19.7 | 0.31 | 43.5 | 13.0 | 9.1 | 0.33 | 0.07 | 0.07 |
| Ni (mg/kg)    | 0.91 | 0.74 | 0.33 | 0.006 | 0.48 | 0.33 | 0.12 | 0.01 | 0.005 | 0.007 |

#### Table 7. Heavy metal migration data of 50Cr15MoV material samples

| Sample number | S1 | S2 | S3 | S4 | S5 | S6 | S7 |
|---------------|----|----|----|----|----|----|----|
| Cr migration mg/kg | 83.8 | 72.3 | 79.4 | 0.05 | 1.6 | 0.08 | 2.18 |
| Ni migration mg/kg | 1.8 | 2.2 | 2.4 | 0.009 | 0.03 | 0.003 | 0.04 |

The data in Table 6 and Table 7 show that the difference in heavy metal migration between the same materials is also very large. These two materials are widely used in kitchen utensils, and the migration test results of heavy metals fluctuate greatly from low to high, and the high content results even exceed the national standard. This phenomenon may be affected by the heat treatment process and microstructure of the material.

### 3.4. Comparative analysis of metallographic microstructure

Combined with the comparison results of 3.3, a sample with a lower migration amount and a higher migration amount was selected from the 30Cr13 material, and the 50Cr15MoV material performs the same operation. The metallographic microstructure was examined separately, and the results of the test were as shown in Fig. 1.
Figure 1. Metallographic microstructure comparison

The graph a and the graph c correspond to lower heavy metal migration, and the samples corresponding to graph b and graph d have very high heavy metal migration. Comparing with the metallographic diagram, it is found that the structure of the graph a and the graph c are relatively uniform and dense, and the metal elements are not easily migrated. The metallographic structure of graph b is larger in grain size, the martensite structure is coarser, and the density and uniformity are poor. Graph d shows that there are undissolved bulk eutectic carbides, which are banded segregation and strip-like non-metallic inclusions, which is also an important factor leading to unstable metal elements and easier migration.

4. Conclusion
(1) There is no linear correlation between the migration of stainless steel and its corresponding content of this element. The microstructure of stainless steel has a great influence on the migration amount, and the migration of austenitic stainless steel is significantly less than that of martensite.

(2) The migration amount of different materials is quite different. Samples of the two materials, 30Cr13 and 50Cr15MoV, are more prone to migration than the national standard., and the migration of samples of 20Cr13 and 30Cr14 is relatively low.

(3) The difference in heavy metal migration between the same materials is also very large, which is closely related to the metallographic structure of the product. The metallographic structure corresponding to the product with low heavy metal migration is uniform and dense, and the corresponding structure of the product with high heavy metal migration is coarser, and the density and uniformity are poor. Therefore, the microstructure of the product has a great influence on the migration of heavy metals.

Acknowledgments
This work was financially supported by Science and Technology Project (NO.2017ZPZ06) of Guangdong quality Supervision Bureau.
References

[1] National Health and Family Planning Commission of the People's Republic of China, GB 4806.9-2016, Chinese National Standards, Chinese, 2016.

[2] National Health and Family Planning Commission of the People's Republic of China, GB 5009.156-2016, Chinese National Standards, Chinese, 2016.

[3] National Health and Family Planning Commission of the People's Republic of China, GB 31604.1-2016, Chinese National Standards, Chinese, 2016.

[4] National Health and Family Planning Commission of the People's Republic of China, GB 31604.49-2016, Chinese National Standards, Chinese, 2016.

[5] ISO, ISO 8442-1:1997, materials and articles in contact with foodstuffs-cutlery and table hollowware-part 1: requirements for cutlery for the preparation of food, ISO standard, 1997.

[6] Jinshan Pang, Factors Affecting the Migration of Harmful Elements in Stainless Steel Food Containers, J. Inspection and Quarantine. 17(2007)75-77.

[7] Huibo Chen, Yikui Jiang, Influencing factors and quality control of chromium ion migration in stainless steel meals and kitchen utensils, J. Modern Food Science and Technology. 26 (2010)1309-1313