Study on the Influence of the Migration of Heavy Metals in 50Cr15MoV Kitchen Knives

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Abstract. 25 batches of 50Cr15MoV kitchen knives were analyzed by chemical composition analysis, surface roughness testing, corrosion resistance testing, metallographic examination, scanning electron microscopy. The results show that: (1) there is no linear relationship between the heavy metal migration of 50Cr15MoV kitchen knives and its corresponding element content, and there is no correlation between the heavy metal migration and the surface roughness; (2) The heavy metal migration of kitchen knives is significantly correlated with corrosion resistance, and the heavy metal migration is positively correlated with the corrosion points in statistics; (3) The heavy metal migration of the kitchen knives with the same material of 50Cr15MoV varies greatly, which is closely related to the microstructure of the kitchen knives. The morphology and distribution of carbide microstructure and the heat treatment process of products have great influence on the heavy metal migration of kitchen knives.

1. Introduction
Stainless steel kitchen knives have the advantages of high wear resistance, rust resistance and durability, and easy cleaning. They have become indispensable kitchen utensils in modern families. But in recent years, the safety of stainless steel kitchen knives has attracted more and more attention. When stainless steel is in contact with acidic food media due to its chemical material, heavy metal ions such as nickel (Ni) and chromium (Cr) are precipitated, which are then absorbed by the human body and slowly accumulate. When a certain limit is reached, it will endanger health. Therefore, GB 4806.9-2016 [1] stipulates the limit index of chromium and other elements, and the European Union and other countries and regions also limit the migration of heavy metals in stainless steel kitchenware.

In recent years, research on the migration of heavy metal elements in stainless steel tableware has attracted much attention. Pang Jinshan, Ying Xiaohong and others [2-6] studied the influence of chemical composition, microstructure, processing deformation and soaking conditions of stainless steel materials on their heavy metal migration, and evaluated them as food contact materials. This study selected 25 batches of 50Cr15MoV stainless steel kitchen knives in the market, and tested the migration of the samples according to the test method of the above national standards, and obtained the migration amount of nickel (Ni) and chromium (Cr) elements, then through the chemical composition, surface roughness, corrosion resistance and microstructure testing, study the factors affecting the migration of heavy metals in kitchen knives, so as to provide reference for the production and use of stainless steel kitchen knives.
2. Test Conditions

2.1. Heavy Metal Migration Test
25 batches of 50Cr15MoV kitchen knives were immersed in food contact materials according to the standards GB 5009.156-2016 [7] and GB 31604.1-2016 [8] to determine the area and volume of the immersion, boiled with 4% acetic acid for 30 minutes, then soaked at room temperature for 24 hours. Repeat the soaking for three times, and take the third soaking solution for heavy metal migration test. The migration of heavy metals was measured using an inductively coupled plasma mass spectrometer (Agilent, ICPMS-7900, USA) to obtain the migration of nickel (Ni) and chromium (Cr).

2.2. Chemical Composition Test
Tested with a floor-standing MAXX metal analysis spectrometer made by German Spike. Test 3 positions for each sample and take the average.

2.3. Surface Roughness Test
The test is carried out according to the standard GB/T 15067.2-2016 [9], and the test instrument is TRIMOS TR precision roughness tester. Test 3 positions for each sample and take the average.

2.4. Microstructure Examination
Metallographic structure examination is carried out according to the standard GB/T 13298-2015 [10]; ZEISS EVO 18 scanning electron microscope was used to observe the micro morphology.

2.5. Corrosion Resistance Test
According to the standard ISO 8442-1:1997 [11], the blade was periodically immersed in a sodium chloride solution at 60°C and a concentration of 1% for 6 hours, and then the corrosion points of the blade were observed and counted.

3. Test Conditions

3.1. Test of Heavy Metal Migration
After testing, the migration results of the heavy metal elements nickel (Ni) and chromium (Cr) of 25 batches of kitchen knives are shown in Table 1. “NA” means the element is not detected. It shows that the amount of heavy metal migration of kitchen knives with the same 50Cr15MoV steel grade varies greatly. Such as Cr migration, the minimum is 0.021 mg/kg, and the maximum is 95.04 mg/kg.

Table 1. Heavy metal migration test results of kitchen knives.

| Sample number | Cr migration mg/kg | Ni migration mg/kg | Sample number | Cr migration mg/kg | Ni migration mg/kg | Sample number | Cr migration mg/kg | Ni migration mg/kg |
|---------------|--------------------|--------------------|---------------|--------------------|--------------------|---------------|--------------------|--------------------|
| GA            | 2.03               | 0.0284             | B1            | 0.116              | <0.002             | B2            | 0.0243             | NA                 |
| GT            | 4.74               | 0.197              | A1            | 0.0248             | 3.65×10^4          | B4            | 0.0263             | NA                 |
| GU            | 1.46               | 0.056              | A2            | 0.0365             | 3.66×10^4          | GC            | 2.45               | 0.102              |
| GW            | 1.39               | 0.021              | C2            | 0.0321             | NA                 | WH            | 0.022              | NA                 |
| GFF           | 95.04              | 1.94               | C4            | 0.0234             | NA                 | E2            | 0.0375             | NA                 |
| GHH           | 0.17               | 3.67×10^-3         | E1            | 2.54               | 0.0987             | F1            | 1.72               | 0.0631             |
| GE            | 0.0473             | <8.0×10^-4         | F2            | 0.599              | 0.599              | WJ            | 0.0488             | <8.0×10^-4         |
| WI            | 2.25               | 0.029              | WF            | 0.028              | NA                 | WG            | 3.11               | 0.0632             |
| WK            | 0.021              | NA                 |               |                    |                    |               |                    |                    |

3.2. Chemical Composition Test
The requirements of GB/T 3280-2015 [12] for 50Cr15MoV steel are shown in Table 2. After testing, the chemical composition of all samples meet the standard requirements. The composition difference
of each sample is very small, but the migration amount of heavy metals is very different, indicating that there is no linear relationship between the migration amount of heavy metal of the kitchen knives and the content of the corresponding element.

**Table 2.** Chemical composition requirements of 50Cr15MoV steel (%)

| Steel grade | C    | Si   | Mn   | P    | S    | Cr   | Mo   | V    |
|-------------|------|------|------|------|------|------|------|------|
| 50Cr15MoV   | 0.45~0.55 | ≤1.00 | ≤1.00 | ≤0.040 | ≤0.015 | 14.00~15.00 | 0.50~0.80 | 0.10~0.20 |

3.3. Surface Roughness Test

After test, the surface roughness value of the kitchen knives is distributed between 0.10 µm and 0.35 µm. The relationship between the surface roughness of the kitchen knives and the amount of Cr migration is shown in Figure 1. It can be seen from the figure that the amount of Cr migration of the sample has no correlation with its surface roughness.

![Figure 1. The relationship between chromium migration and surface roughness](image)

3.4. Microstructure Examination

Select E2, GU, and GFF sample with low, medium and high heavy metal migration from the samples, examine their metallographic structure and non-metallic inclusions, and conduct scanning electron microscope observations to discuss the mechanism of heavy metal migration from the microstructure.

3.4.1. Metallographic structure microscopy

Figure 2 shows the metallographic structure of three kitchen knives. The corrosive agent is 15ml HNO₃+30ml HCl+50ml H₂O solution. The figure shows that the metallographic structure of the three is fine needle tempered martensite + hidden needle tempered martensite + granular carbide + retained austenite. The microstructure of the E2 sample is relatively uniform, but contains a small amount of massive carbides. The carbides of the GU sample are many and fine, and there is a slight band segregation of massive carbides. Part of the grain boundaries of the GFF sample are straight and coarse, it shows a phenomenon of heat treatment overheating; it also shows that the GFF sample has a lot of massive carbides, some are distributed in bands, and most of the large carbides are surrounded by small corrosion.
3.4.2. Scanning electron microscope inspection

Figure 6 is SEM images of the three samples. It shows that the carbides of the E2 sample are relatively uniform, and the diameter is mostly 1 μm to 2 μm. The carbides contained in the GU samples are not uniform, most of the carbides have a diameter of 1 μm to 2 μm, and some of the bulk carbides with a larger diameter of about 3 μm exhibit band-like segregation. The carbide diameter of GFF sample is about 2 μm, and there are more carbides at the intersection of grain boundaries.

3.4.3. Detection of non-metallic inclusions

Figure 4 shows the non-metallic inclusions of E2, GU, and GFF sample. It shows that the non-metallic inclusions contained in the E2 and GU sample are mainly spherical oxide inclusions, with grade D1.5 and D1 of the fine system respectively. GFF sample is mainly sulfide inclusions with grade A0.5 of the fine system. It shows that the contents of non-metallic inclusions in the three kitchen knives is relatively less.

Combined with the analysis of metallography and SEM photos, the carbides of GU and GFF sample are distributed in bands. In the area where carbon and alloying elements are enriched, the melting point of steel decreases. This area is prone to overheat during heat treatment process, and the solubility of carbon and alloying elements in the austenite decreases, and make the hardness after quenching is reduced, resulting in a large structure stress between the carbon and alloy elements enrichment region and poor region, which reduces the corrosion resistance, and chromium ions are
easier to precipitate and produce higher migration. Therefore, GU and GFF samples have higher heavy metal migration than E2 sample.

In addition, the heat treatment overheating phenomenon of GFF sample causes the chromium in the matrix migrate more to the grain boundary and combine with carbon to form chromium carbides, resulting in the occurrence of a chromium-poor area near the grain boundary, which makes the grain boundaries easier to be corroded, reduces the corrosion resistance of the material, and greatly increases the migration of heavy metals.

3.5. Corrosion Resistance Test

Figure 5 shows the photos of the above 3 kitchen knives samples after corrosion resistance test. It can be seen that E2 sample with low heavy metal migration and GU sample with medium heavy metal migration have few corrosion points, while GFF sample with high heavy metal migration have many corrosion points.

![Figure 5. Photos after the corrosion resistance test of the kitchen knives (a) E2; (b) GU; (c) GFF](image)

In order to study the relationship between corrosion resistance and heavy metal migration more clearly, the number of corrosion points after the corrosion resistance test of 25 batches of samples is counted. The corrosion points are particularly dense and are counted as integers. The relationship between Cr migration results and corrosion points is showed in Figure 6.

![Figure 6. Relationship between chromium migration and corrosion points after corrosion resistance test](image)
Figure 6 shows that the Cr migration of kitchen knives increases with the increase of the number of corrosion points, indicating that the heavy metal migration has a greater correlation with corrosion resistance, and the heavy metal migration is statistically positively correlated with the number of corrosion points. This is because the more corrosion points of the kitchen knives, the more serious the corrosion, and the easier the chromium ion in the kitchen knives is to precipitate.

4. Conclusion
(1) There is no linear relationship between the heavy metal migration of 50Cr15MoV kitchen knives and its corresponding element content. There is no correlation with its surface roughness.
(2) The heavy metal migration of kitchen knives is highly correlated with corrosion resistance, and the heavy metal migration is positively correlated with the number of corrosion points in statistics.
(3) The heavy metal migration of the kitchen knives with the same material of 50Cr15MoV varies greatly, which is closely related to the microstructure of the kitchen knives. The morphology and distribution of carbide microstructure and the heat treatment process of products have great influence on the heavy metal migration of the kitchen knives.

5. References
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[11] GB/T 13298-2015 Inspection methods of microstructure for metals (Standardization Administration of the P.R.C)
[12] GB/T 3280-2015 Cold rolled stainless steel plate, sheet and strip (Standardization Administration of the P.R.C)