

# 取代装饰铬的纳米 Sn-Co-X 合金

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**摘 要:** 装饰铬在全世界的市场需求量是硬铬的 3 倍, 长期以来镀铬工艺是众所周知的有毒工艺, 由于电镀纳米 Sn-Co-X 合金具有与  $\text{Cr}^{6+}$  非常接近的颜色及更好的耐腐蚀性, 且对环境和人体安全, 是取代  $\text{Cr}^{6+}$  与  $\text{Cr}^{3+}$  的极好选择。纳米 Sn-Co-X 的耐腐蚀性优于  $\text{Cr}^{6+}$  和  $\text{Cr}^{3+}$ , 更优于常规晶态的 Sn-Co 合金。用扫描电镜 (SEM)、透射电子显微镜 (TEM)、X 射线光电子能谱仪 (XPS) 和原子发射光谱 (AES) 对纳米 Sn-Co-X 合金的微观结构及腐蚀前后的表层变化进行了分析, 阐述了纳米 Sn-Co-X 合金优异的耐腐蚀性机理。

**关键词:** 纳米晶粒; Sn-Co-X 合金; 替代装饰铬镀层; 镀铬

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## Nano-crystalline Sn-Co-X Alloy Alternative to Decorative Chromium Plating

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**Abstract:** Decorative chromium demand in the worldwide market is more than three times of hard chromium. However, chromium plating process has long been known to be hazardous. The corrosion resistance of nano-crystalline Sn-Co-X alloy intended as an alternative for decorative chromium has been studied. The corrosion resistance of Sn-Co-X is better than trivalent chromium and hexavalent chromium, and it is much better than coarser gained Sn-Co alloy. The microstructures of Sn-Co-X alloy were analyzed by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) and atomic emission spectrometry (AES) before and after corrosion. The mechanism of its excellent corrosion resistance was described.

**Key words:** nano-crystalline; Sn-Co-X alloy; alternative decorative chromium; chromium plating

## 0 Introduction

The chromium plating process has long been known to be hazardous. However, studies in the last decade have known it to be particularly dangerous, especially for workers in chromium plating facilities [1].

In response to growing health concerns, the U. S Environmental Protection Agency (EPA) began to regulate emissions into the air of chromium, citing strong evidence that chromium causes lung cancer and other serious conditions. The compliance deadline for the EPA's new plating and pol-

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ishing area sources rule was set to go into effect on July 1, 2010 for non-chromium electroplating, electropolishing, electroforming, electroless plating, thermal metal spraying, chromate conversion coating, coloring, mechanical polishing of metals and formed products.

For more than forty years, academic and industrial researchers from all over the world have taken a strong interest in alternative processes for hard chromium and decorative chromium. Among them, nanotechnology is the most promising. The nanograined micro-structure has been found beneficial in imparting resistance against localized corrosion in the acidic environment. For example, superior localized corrosion resistance in HCl was observed for nano-crystalline Ni-Co-X alloy<sup>[2]</sup>. Similar observation of improved resistance against intergranular corrosion in the acidic environment has been reported for electrodeposited nano-crystalline Ni and Ni-P alloy<sup>[3-4]</sup>.

Decorative chromium demand in the worldwide market is more than 3 times of hard chromium (MYM15.91 billion in 2003). There are, however, no reports of nano-crystalline Sn-Co alloy for decorative application. This paper represents a new potential application for nanotechnology. To evaluate the corrosion and tarnish resistance of nano-crystalline Sn-Co-X alloy, comparison tests were performed among the well-known chromium coating and coarser-grained Sn-Co alloy.

## 1 Experiments

The corrosion resistance was performed under the conditions of CASS (ASTM B368 or, ISO 17025). Brass flat panels of 6.99 cm × 10.16 cm were polished with SiC sandpaper (12.36 μm) and MgO powder. They were etched in 10% H<sub>2</sub>SO<sub>4</sub> at room temperature for 0.5~1.0 minutes and rinsed with distilled water. The plating processes are listed in Table 1. The specimens were then thoroughly rinsed with distilled water and dried by cool air blast after plating. METTEX13 (M13), a nano-crystalline Sn-Co-X alloy, was patented by Shining Surface Systems, Inc. (3S). A JEOL 6301F SEM was used to study the morphology. A FEI TECNAI G<sup>2</sup>

20 TEM was used to study the morphology and micro-structure. The X-ray photoelectron spectroscopy (XPS) measured was made on ULVAC - PHI PHI quantera scanning X-ray microprobe at 15kV and 25W. The atomic emission spectrometry (AES) measured was made on ULVAC - PHI PHI 700 scanning auger nanoprobe. Survey and high resolution XPS spectra were generated with the analyzer pass energy setting at 280 eV and 55 eV, respectively. The voltage and current of the electron beam for AES analysis were 5 kV and 10 μA, respectively. An argon ion gun with a voltage of 2 kV, an emission current of 15 mA, and scan area of 2 mm × 2 mm were used for depth profiling study. The sputter rate for SiO<sub>2</sub> is 10 nm/min.

## 2 Results

Chromium plating has been developed for various decorative and domestic purposes for its excellent corrosion resistance, tarnishing resistance and beautiful appearance-white with blue hue. Tin-Co-balt alloy plating is almost the same color (white with dark blue hue) as chromium plating<sup>[5]</sup>. It is very difficult to distinguish the appearance color from chromium and Sn-Co-X alloy if adding appropriate II B group elements in So-Co alloy solution.

### 2.1 Corrosion resistance of nano-crystalline M13 (Sn-Co-X)

The results of CASS test of M13 compared to the third generation of trivalent chromium, hexavalent chromium and coarser gained Sn-Co, are shown in Table 1. The corrosion resistance of nano-crystalline M13 is better than trivalent chromium and hexavalent chromium, and it is much better than coarser gained Sn-Co alloy.

### 2.2 XPS and AES investigation of nano-crystalline M13

The composite elements were analyzed by XPS and AES before and after sputtering through Ar<sup>+</sup> beam (SPT). For the nano-crystalline Sn-Co-X (M13) plating coatings, survey spectra of XPS show that Sn, Co, C, and O exist as shown in Fig. 1. The AES results also suggest the existence of Sn, Co, O, and C. After 0.5 minutes of Ar<sup>+</sup> SPT, the C

表 1 CASS 试验结果  
Table 1 Results of CASS Test

	Cr <sup>3+</sup>	Cr <sup>6+</sup>	Cr <sup>3+</sup>	Cr <sup>6+</sup>	Sn-Co	M13
Semi-bright nickel	~22 μm	~22 μm	~22 μm	~22 μm	~22 μm	
High sulfur nickel	~1.5 μm	~1.5 μm				
Bright nickel	~11 μm	~11 μm	~11 μm	~11 μm	~11 μm	
Microporous nickel			~1.5 μm	~1.5 μm	~1.5 μm	
Noble nickel	~1.5 μm	~1.5 μm				
M8(Nano-Ni-Co-B)						(7+10) μm
Sn-Co(Coaser-gained)					~1 μm	
Trivalent chromium	~0.3 μm		~0.3 μm			
Hexavalent chromium		~0.3 μm		~0.3 μm		
M13(Nano-Sn-Co-X)						(1.5+1.5) μm
CASS rating for 24 hours	10	10	10	10	10	10
CASS rating for 48 hours	8	8	10	10	10	10
CASS rating for 96 hours			9	9	9	10
CASS rating for 120 hours			9	8	8	10
CASS rating for 144 hours			7	7	7	10
CASS rating for 168 hours						9

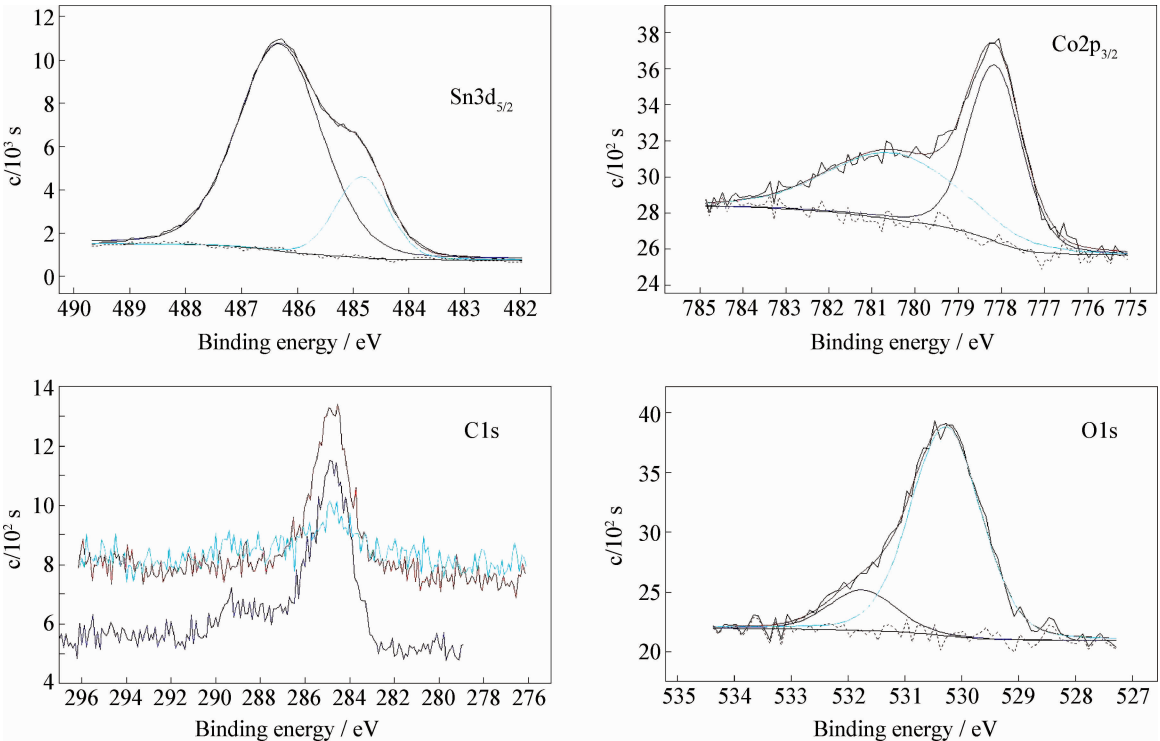


图 1 纳米 Sn-Co-X(M13)合金元素的结合能  
Fig. 1 Binding energy of elements in nano-crystalline Sn-Co-X (M13) alloy

band disappeared, which suggests that carbon mostly exists in the contamination of the coating surface. Figure 2 shows the composition of the coat at different sputtering times through AES depth profiling

technique. The relative atomic content fractions (AC%) of the elements were calculated by computer. The composition of the coating was stable after 0.5 minutes of SPT. With the reference of SiO<sub>2</sub> and

the SPT speed of 10 nm/min, the atomic percentages in the median stable area during the SPT are 32.58% Sn, 62.68% Co, and 4.80% O.

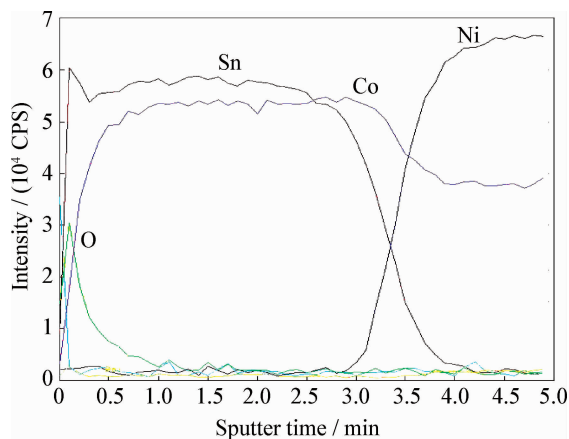


图 2 纳米 Sn-Co-X(M13)合金元素分析

Fig. 2 Composition depth profiling of the nano-crystalline Sn-Co-X (M13) alloy coating

High resolution XPS of the nano-crystalline Sn-Co-X alloy coating is shown in Fig. 1. The binding energies of Sn 3d before and after SPT are shown in Fig. 1. The peaks at 484.84 eV and 486.32 eV indicate that tin exists in oxidation states of  $2^+$  and 0 both the surface and the interior. Cobalt exists in oxidation states of  $2^+$  and 0 both the surface and the interior, because two different binding energies of 778.15 eV and 780.50 eV of  $\text{Co}2p_{3/2}$  before and after SPT appear. No nickel before SPT and  $\text{Ni}^{3+}$  ( $\text{Ni}_2\text{O}_3$ ) and  $\text{Ni}^{2+}$  ( $\text{NiO}$ ) after SPT indicates nano-crystalline Ni-Co-B alloy under top layer nano-crystalline Sn-Co-X (M13) alloy. The binding energies of Oxygen 1s before and after SPT are 530.28 eV and 531.75 eV, respectively, which indicates Oxygen exists in the oxidation state of 2 both the surface and inner coating. The very interested thing was that Oxygen on the surface was 7–8 nm using the sputter rate of  $\text{SiO}_2$  as a reference. It is much thicker than that of coarser grained Sn-Co's 6.7–10.4 Å<sup>[6]</sup>, because the sputter rate of Au can be about 5 times higher than that of  $\text{SiO}_2$ <sup>[7]</sup>.

### 2.3 SEM and TEM investigation of nano-crystalline M13

To explore the reasons why nano-crystalline Sn-Co-X (M13) alloy shows such excellent corro-

sion resistance, the following analyses were carried out. Figure 3 shows the nano-crystalline M13 surface morphology, whose surface is smooth, no porosity and cracks.

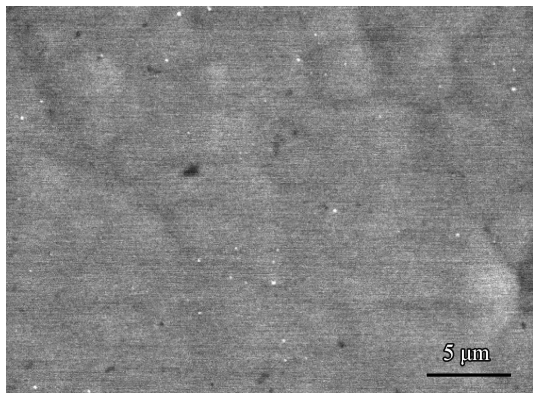
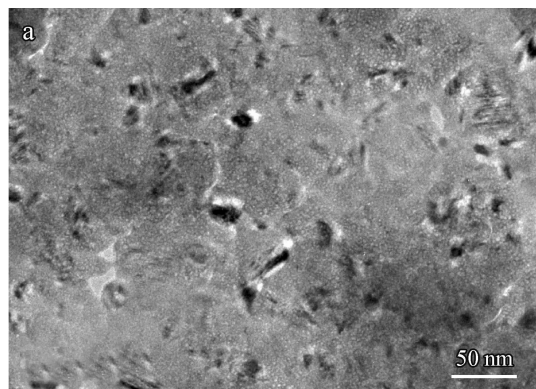


图 3 纳米 Sn-Co-X(M13)合金 SEM 形貌图

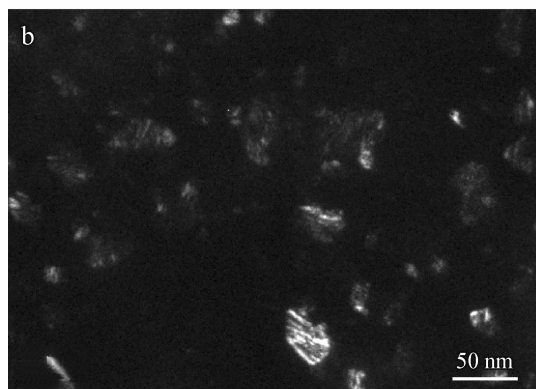
Fig. 3 SEM of nano-crystalline Sn-Co-X (M13) alloy

Figure 4 shows the TEM morphology of nano-crystalline Sn-Co-X (M13) alloy. Many finely dispersed precipitates about 6–8 nm in size are presented in the matrix. The selected area diffraction pattern show diffraction rings characteristics of a multi-crystal structure, as shown in Figure 5. The distribution of spots on the rings suggest that the main contribution to this diffraction pattern arises from an ordered hexagonal structure with a lattice constant of  $a = 0.528$  nm and  $c = 0.426$  nm, which is CoSn alloy. The grain size of the matrix is so small that the grain boundaries are invisible; therefore it is difficult to determine the grain size through the dark field image method. Using the micro-beam diffraction method instead, at least four sets of diffraction patterns could be observed when the diameter of the electron beam was about 4 nm. In the view of this, the grain size can be estimated as being 2.5 nm.

Based on studies above, it can be concluded that the structure of nano-crystalline Sn-Co-X (M13) plating coatings consists of an amorphous matrix that includes some nano-crystals containing dispersed CoSn inter-metallic compound. The grain size of nano-structure in the matrix is about 2.5 nm and the inter-metallic compound was 6–8 nm.



(a) Bright field



(b) Dark field

图 4 纳米 Sn-Co-X(M13)合金的 TEM 形貌

Fig. 4 TEM of nano-crystalline Sn-Co-X (M13) alloy

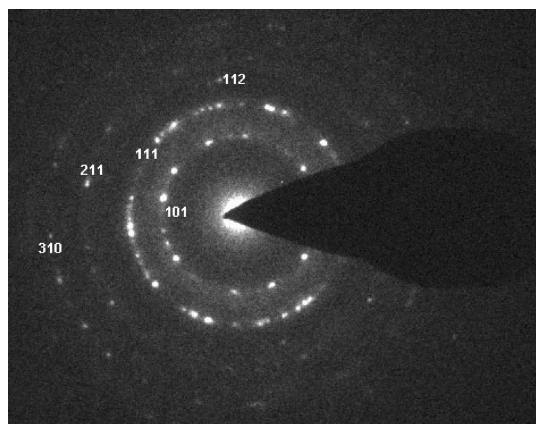


图 5 纳米 Sn-Co-X(M13)合金的选区衍射图

Fig. 5 Selected area diffraction pattern of nano-crystalline Sn-Co-X (M13) alloy

### 3 Conclusions

(1) The nano-crystalline Sn-Co-X (M13) plating alloy coating is intended as an alternative to decorative chromium, showing similar color and ex-

cellent corrosion.

(2) The corrosion resistance of the nano-crystalline Sn-Co-X(M13) plating alloy coating is related closely to its microstructure:

a. Nano-crystalline Sn-Co-X (M13) plating coating consists of an amorphous matrix that includes some nano-crystals containing dispersed CoSn inter-metallic compound. The grain size of nano-structure in the matrix is 2.5 nm and the inter-metallic compound is 6-8 nm.

b. Nano-structure and amorphous structure can significantly reduce its sensitivity to localized corrosion.

c. The absorbed oxygen of the nano-crystalline Sn-Co-X(M13) plating alloy coating is higher than coarser grained Sn-Co. The absorbed oxygen can prevent the dissolution of the metal coating, thus promoting the growth of the passive film and in turn increasing its stability.

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