MOLTEN SALT AND SLAG IN ANCIENT CHINA [1]

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ABSTRACT

This paper deals with molten salt and slag in ancient China. The following fields are discussed: copper smelting, bronze melting and casting, bronze weapons manufacturing, iron smelting, glaze and glass making. Some important archaeological discoveries are also describled.

Key words: molten salt slag ancient China

1 INTRODUCTION

Over the past 50 years, there has been an increase in research on archaeometallurgy, i.e., the study of metal and alloy production in ancient China, due to the facts that many valuable old metal vessels, painted potteries, mirrors and swords have been excavated or unearthed by archaeologists, and that copper and iron slags, solidified salts, glazes and glasses have been found in ancient mining and metallurgical sites and foundry remains.

This paper is based on literature written by scientists[1,2] and medicinists[3] in ancient times as well as books written by modern metallurgists[4,5]. The most important information is from archaeological data obtained by Chinese archaeologists.

2 MOLTEN SALT AND SLAG IN ANCIENT CHINA

2.1 *Copper Smelting*

Copper smelting remains at the ancient sites of Tonglushan, Hubei Province, have been excavated since 1972. The remains are dated back to the years of 770 ~ 475 B. C.. The site occupied an area of 2 km^2. In the neighborhood of the ancient mines, ruined copper, smelting shaft furnaces, copper ores, iron ores and charcoal were found. The copper ores which contain 20 ~ 50 wt.-% malachite were the raw material for Cu production. Iron ores were used for making slags. Charcoal was used as a reducing agent and fuel in the process. A thick layer of copper slag(about 400,000t)was found in the vicinity of the smelting furnaces. The slag was black in coluor and thin plates in form. Its surface was smooth or with the appearance of ripples. Its fracture have a dense, glassy form. The chemical analysis of more than 100 samples revealed that the mole ratio of $CaO:(SiO_2+FeO)$ is 1.0 ~ 1.3, the copper content is 0.4 ~ 1.3wt.-%(average 0.7wt.-%), the melting point is in the range of 1,100 ~ 1,200℃, the density is 3.5 ~ 4.0 g/cm^3, the viscosity is 0.2 p.s. at 1,280℃. It is suggested that the furnace was supplied with forced drafts and the slag might have high fluidity at high temperature. Copper cakes excavated there contain Cu about 94wt.-% and Fe < 5.4wt.-%.

2.2 *Bronze Smelting and Casting*

In the old tombs and ancient bronze melting and casting remains, many bronze vessels

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and articles were unearthed. They include

(1) Bronze Cup [1]

Old copper smelting furnaces, copper slags and bronze vessels were discovered from Erlitou remains [2], which was an important bronze smelting centre in the early Shang Dynasty.

(2) Simuwuding [3]

In the late Shang Dynasty the old bronze technology reached a high level. From the remains at Anyang [4], bronze vessels, copper and iron ores, and smelting furnaces have been excavated since 1929. The famous simuwuding made in the last Shang Dynasty was unearthed in 1939. It was 133 cm high, 116 cm long, 75 cm wide and 875 kg in weight. It was made of Cu 84.77wt.−%, Sn 11.84wt.−%, Pb 2.76wt.−%, and balances 0.8wt.−%, and cast piece by piece and then joined together by casting.

(3) Bronze Bells [5]

In ancient China bronze bell series were the chief musical instruments on ceremonies and festivals, and bells and dings [6] were regarded as symbols of authority and dignity. In the past 40 years, over 40 bells series have been excavated. Among them the bell series unearthed from the tomb of Zenghouyi in Sui county [7] of Hubei Province was most prominent. There were 65 bells in one series, placed in 3 rows. Its total weight was 2,500 kg. It was made in the early Warring States Period and was regarded as a representative of ancient Chinese culture. It was made of pure metals and cast in clay moulds, with an elegant style and beautiful musical sound. It contains Sn 13 ~ 16wt.−%, Pb 1 ~ 3wt.−%, Cu rest.

(4) Transparent Mirror [8]

The Shanghai Museum keeps a transparent mirror excavated from one tomb of Han Dynasty. The Chinese characters cast on the backside of the mirror can be seen under sunshine or strong light.

Several books mention the preparation technology of bronze alloys. Ref.[6] states that both copper and tin are mild, but a strong material is obtained when combining these two mild metals. Ref.[7] describes the compositions of eight alloys. Where did the metals come from? Ref.[8] states the metals were from the south. In Qin Dynasty, Li Shi[9] mentioned that copper and tin were from the south [9], i.e. from Guangxi, Yunnan and other provinces. Ref.[10] describes the four factors for making good foundry articles. These conclusions were reached from the metallurgical practices in ancient China. Salt may have been used as flux, and molten salt may have been formed during the melting and casting operation of metals and alloys.

Foundry remains were excavated in Yinxu [10] in Anyang city, which was the capital of the late Shang Dynasty. This ancient site occupied an area of 10,000 m^2. Broken crucibles and copper salgs were found there. The copper slag, which is green in color, was formed while melting the bronze alloy with the addition of charcoal and flux(salt peter) for protection from oxidation. The charcoal was added to produce a reducing atmosphere on the molten metal surface and to supply heat energy for oxidation. The flux might have been salt peter which can be obtained from the ground surface. After burning in air, the ash in the charcoal formed alkali oxides which could be used as flux. The use of flux was confirmed by the fact that the inside wall of the crucible for melting the bronze was corroded and was covered with a layer of copper slag. Bronze vessels were cast after melting copper and tin together in the crucibles. There were big melting

1 铜爵 2 河南偃师县二里头遗址; 3 司母戊鼎; 4 河南安阳殷墟; 5 青铜编钟; 6 钟、鼎; 7 湖北随县曾侯乙墓编钟; 8 透光镜; 9 南金; 10 殷墟 [6] 吕不韦.吕氏春秋·别类篇; [7] 考工记; [8] 诗经·鲁颂; [9] 李斯.谏逐客令; [10] 荀子

furnaces with diameters up to 1 m. Small crucibles were also used for melting bronze as well as for transporting the molten bronze to the mould.

2. 3 *Bronze Weapons Manufacture*

(1) Goujian Sword [1]

In 1965, one ancient sword, which belong to King Goujian [2] of Yue State, 2,300 years ago, was excavated. It is still bright and sharp now. The knife edge contains(wt.−%) Cu 80.3, Sn 18.8, Pb 0.4. The length of the sword is 55.7cm.

(2) Qin Sword [3]

In 1974, Qin Swords were excavated from the No. 1 warriors and horses pit of Emperor Qin's tomb. The Qin swords were made about 200 years late than the Goujian sword. The bronze swords were about 94 cm long. Although the Qin swords were buried underground in wet conditions for more than 2,100 years, they had not rusted or corroded, and are still bright and sharp, and can be used to cut 19 newspapers piled together. It was reported that the blade of the sword was covered with a thin layer(10 ~ 15 μm thickness) of chromium oxide.

(3) Qin Arrowhead [4]

Bronze arrowheads were excavated from the No. 1 warriors and the horses pit of Emperor Qin's tomb These bronze arrowheads are black in color and rustless. Ke Jun [5] *et al* carried out metallographic and electron scanning studies. They found that there is a layer of dense oxide which is about 2% chromium and protects the lower layer without chromium. This shows that this black oxide layer was made by coating the bronze with an artificially prepared chromium−containing oxide. The following explanation has been proposed: in modern technology, the surface of bronze and other nonferrous metals and alloys are usually treated with aqueous chromate or dichromate solutions. But in ancient times, where did the chromium salts come from? They may have been prepared by reacting chromium−containing ore with molten salt peter(KNO_3) at 800 ~ 1,000 °C, then leaching the sinter−product with water to produce chromate or dichromate solution. The same explanation may be also applied to Qin swords.

2. 4 *Arsenic Bronze Preparation*

Ref.[11] presented a method of preparing arsenic bronze. White arsenic oxide(As_2O_3) was mixed with dates to form small briquets and put into copper liquor. Then, the salt peter(KNO_3) was added to form a molten slag. After deslagging, arsenic bronze was obtained. During the smelting, As_2O_3 was reduced to As by carbon formed when the dates were burned at high temperature. Then, As combined with Cu to form arsenic bronze. Salt peter was used to form a molten salt which collected the oxides formed in the process.

From the above, it is understood that salt peter was a salt used to form a molten salt for bronze casting and later for white bronze manufacturing to form molten salt in ancient China up to the Shang Dynasty. So the famous medicinist Li, Shizhen in his book[3] described the salt peter in considerable detail.

2. 5 *Iron Smelting*

The present-day Henan Province was an important region in which many of Han Dynsty ironworks were located and several iron smelting sites were excavated. Excavations reveal that hearth No. 1 unearthed at Gushing town in Zhengzhou city, represents the remains of a blast furnace. The hearth is oval in shape with a bottom area of 8.5m^2. The fur-

1 勾践剑; 2 越王勾践; 3 秦剑; 4 秦镞; 5 柯俊; [11] 何薳·春渚纪闻

nace has an estimated volume of about 50 $m^3$and a daily production of 0.5 t pig iron. It is also noteworhty that limestone was used as flux and charcoal as fuel / reducing agent at the iron smelting. From the appearance of iron slag in glassy or massive form in the sites, it seemes that the slag had good fluidity. The composition of pig iron was C 4.0wt.−%, Si 0.21wt.−%, Mn 0.21wt.−%, P 0.29wt.−% and S 0.091wt.−%.

3 CONCLUSIONS

The molten salt and slag in ancient China were an important part of copper smelting, bronze casting, bronze weapons manufacturing, iron smelting, glaze and glass making. This paper is a survey of ancient and present literature, and archaeological data. The author thinks that similar study should be carried further.

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term behaviour according to the current contraction policy.The ratio of profits kept for enterprises decreased continuously which negatively affected their ability of capital accumulation and the development of enteaprises. All these factors have restricted productivity.

3. 4. 3 The Operation Mechanism of the Enterprise Has Defects

The operation Mechanism is a factor of productivity. In order to reform the inner operation mechanism of the enterprises, which is not proper for the improvement of productivity, the current labour system, personnal system and distribution system must be improved. During recent years, the CNNC established a series of necessary policies, such as connecting salaries with profits and revenues, assigning directors by an objective system, reducing the staff, etc.

All these reforms have had positive effects. However, there still exist many deep seated problems within the enterprises. Optimal mechanisms inside the enterprises should be built; the activity of employeers should be mobilized; and productivity should be improved efficiently.

(To be continued)