

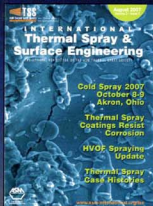
# AMP

ADVANCED MATERIALS PROCESSES®

www.asminternational.org/AMP

AUGUST 2007 • VOLUME 105, NO. 8

INCLUDED IN THIS ISSUE



# MS&T'07

MATERIALS • PROCESSES • APPLICATIONS

AN ASM INTERNATIONAL PUBLICATION



# AMP

ADVANCED MATERIALS & PROCESSES

COLOR CODING IDENTIFIES  
AREAS OF INTEREST

METALS/POLYMERS/CERAMICS

TESTING/CHARACTERIZATION

PROCESS TECHNOLOGY

EMERGING TECHNOLOGY

BUSINESS TRENDS

GLOBAL ECONOMY

**33** Automotive Materials at MS&T'07  
A sampling of automotive materials papers to be presented in Detroit, Mich., during Materials Science & Technology 2007, September 16–20.

**38** Ancient Chinese Bronze Casting  
*Lisa Reiner*  
By 1100 B.C., a high level of artistic and technical mastery in bronze casting had been achieved by early Chinese metallurgists.

**45** Corrosion-Resistant Nickel Alloys — Part 3  
*Paul Crook*  
Ternary nickel alloys provide levels of corrosion resistance not possible with other alloys. This is part three of a four-part series.

**49** Digital Imaging in the Lab  
*Ross Baule*  
Digital imaging and image analysis are now industry standards because they allow a greater range of options than conventional photography.

**55** Instrument Combines SEM and Fatigue Testing  
*Adriana Romero*  
Large-chamber scanning electron microscope can accommodate samples up to 1 m in diameter ... or a servo-hydraulic fatigue testing machine.

**60** Making Med Devices  
ASM's 2007 Materials & Processes for Medical Devices (MPMD) Conference/Expo (September 23–25, Palm Desert, Calif.) is previewed.

**62** Motown Welcomes MS&T'07  
Exhibitor products are featured in this preview of the Materials Science & Technology 2007 Conference and Exhibition (Detroit, Mich., September 16–20). MS&T'07 is co-located with the 24th ASM Heat Treating Society Conference & Exposition (September 17–19).

**69** International Thermal Spray & Surface Engineering  
*iTSSe* is the Official Newsletter of the ASM Thermal Spray Society (TSS). The quarterly supplement focuses on thermal spray and related surface engineering technologies. Its table of contents is on page 71.

**93** ASM News  
ASM Awards Program recipients for 2007 are featured. Another story outlines "The Many Advantages of Hosting an ASM Materials Camp."



On the cover: Photo taken from a Detroit River vantage point shows a portion of the Detroit, Mich., skyline at night (Renaissance Center at right). The Motor City hosts the Materials Science & Technology Conference and Exhibition (MS&T'07) September 16–20. Articles in this issue present technical program highlights (p. 33) and provide a Tour Guide to many of the exhibits to be featured at Cobo Center (p. 62).

## DEPARTMENTS

- 4 Editorial
- 8 Of Material Interest
- 13 Innovations
- 13 Metals/Polymers/Ceramics
- 17 Process Technology
- 20 Testing/Characterization
- 23 Emerging Technology
- 25 Business Trends
- 27 Global Economy
- 105 New Society Members
- 109 Tech Notes
- 111 Stress Relief
- 113 Special Advertising Section
- 114 Calendar
- 114 Products/Literature
- 117 Sales Offices
- 119 Classifieds
- 119 Advertisers Index
- 120 Pastimes

ASM International® is a society whose mission is to gather, process, and disseminate technical information. ASM fosters the understanding and application of engineered materials and their research, design, reliable manufacture, use, and economic and social benefits. This is accomplished via a unique global information-sharing network of interaction among members in forums and meetings, education programs, and through publications and electronic media.

Advanced Materials & Processes (ISSN 0882-7968, USPS 525-0208) is published monthly by ASM International, Materials Park, Ohio 44037-0002, tel: 440/338-5151, fax: 440/338-4834. Periodical postage paid at Norwell, Ohio, and additional mailing offices. Vol. 165, No. 8, August 2007. Copyright © 2007 by ASM International. All rights reserved. Distributed at no charge to ASM members. Subscription: \$798. Single copies: \$33. POSTMASTER: Send 3579 forms to ASM International, Materials Park, Ohio 44037. Change of address: Request for change should include old address of the subscriber. Missing numbers due to "change of address" cannot be replaced. Claims for nondelivery must be made within 90 days of issue. Canada Post Publications Mail Agreement No. 40721015. Return undeliverable Canadian addresses to: PO Box 697 STN A, Windsor, ON, N9A 6N4. Printed by Publishers Press Inc., Stephensville, Ky.



*The Chinese had demonstrated proficiency in hard, thin-walled ceramics by the end of the Neolithic period, and took advantage of these skills to develop casting processes for both simple and complex piece molds.*

# ANCIENT CHINESE BRONZE CASTING

*Lisa Reiner*

*California State University Northridge  
Northridge, California*



Reverse side of mask.

*Fig. 1 — This mask is an example of the bold exaggeration and distortion that sets most of the Chinese bronzes apart from European bronzes. Human mask, late Shang, has height of 40.3 cm, width of 60.5 cm, thickness of 0.6 cm, and weight of 13.4 kg. It was excavated from Sanxingdui Pit II (Sichuan Province), and is the largest intact mask of this type found. Twenty masks of a similar style, characterized by the U-shaped structure when viewed from above, were found in this pit. The ears are pierced for earrings. Close examination by archaeologists led to the conclusion that the mask was completed in a single casting with molds possibly divided vertically at the ears<sup>4,5</sup>.*

The transition from Neolithic pottery to the emergence of metalwork (around 2000 BC) held significance for bronze development in China, where processing techniques sharply contrasted with those in the Middle East and Europe. The piece mold process was more of an extension of ceramic technology than a distinct casting innovation. By 1100 BC, a high level of artistic and technical mastery in bronze casting had been achieved by the Chinese. This was true even though Chinese bronzes showed huge metallurgical variations compared with contemporary European bronze alloys that had far more consistent chemistries.

However, the need to control alloy behavior to provide required properties of the final casting did subsequently lead the Chinese to become accomplished bronze metallurgists. The famous terra cotta soldiers found gripping bronze weapons at Xi'an make obvious the deliberate alloying of copper and tin with titanium, magnesium, and cobalt for superior hardness (~220 BC).

## **Casting techniques**

The Chinese worked pottery during the Neolithic Period (8000 to 1700 BC); the pottery kilns found near Xi'an could maintain temperatures at 1400°C as early as the 6th millennium BC, more than enough to melt copper. They developed the piece mold technique and lost wax method for casting bronze during the Shang dynasty (1700 to 1100 BC). The Shang metallurgical tradition appears to have progressed at a rapid pace, as demonstrated by the detailed and elab-



Fig. 2 — This Taotie pattern block was made from baked clay. It was excavated at the Houma Foundry in Shanxi Province, 18 x 42 cm, (c. 453 BC)<sup>[7]</sup>.

orate decoration on the ritual bronzes (Fig. 1). As well, there is little evidence of an extended transitional phase between the Neolithic and Bronze periods.

Chinese techniques sharply contrasted with those of the contemporary Middle Eastern and European bronze technology, which relied on annealing, cold working and hammering<sup>[1-3]</sup>. The Chinese used simple and composite piece mold techniques for most of their history, while Europeans had developed the lost wax bronze casting as far back as 3500 BC<sup>[3]</sup>. These differing techniques are indications that the bronze industry in China developed independently from Europe<sup>[2]</sup>.

#### Chinese bronze alloys

Bronze is produced when copper combines with tin in various proportions. Many other elements (lead, zinc, aluminum) can be added to create different bronze alloys with specific characteristics and mechanical properties<sup>[6]</sup>. The Chinese became more sophisticated bronze metallurgists due to this preference for casting; attention to the metallurgy became the primary means of controlling the metal behavior. Bronze alloys were used almost to the exclusion of any other alloy for nearly 1000 years in China. Even after the introduction of iron, bronze remained the metal of choice for weapons, vessels, coins, and statuary<sup>[2]</sup>.

In most European or Middle Eastern cultures, metalworking began with native copper, gold, or electrum (an alloy of silver and gold); these were soft metals that could be shaped into sheet. Smelted metal, to the contrary, was not so easily worked into desirable shapes.

The early Chinese took a different approach; instead of the conventional metalworking they cast the copper ores in clay molds. Bronze artifacts initially were rough copies of clay objects<sup>[1, 7, 8]</sup>. As casting technology improved, the cast objects became increasingly sophisticated. Access to superior ceramic technology undoubtedly played a major influence in forming the delicate inscriptions, the ability to properly fit molds together, and preventing them from cracking during the pour<sup>[1]</sup>.

Fig. 4 — This Zun (wine vessel), was cast during the Zhou dynasty, during the 5<sup>th</sup> century BC, at Anyang. Height is 26.5 cm, width is 20.0 cm, and weight is 2.55 kg. This extraordinary zoomorphic creature resembling a bird appears to be cast in a two-piece, four-division mold assembly, with a mold joint down the center of the breast and back. The legs were precast with a clay core, and the body was cast to them. The head is removable with a locking mechanism. The entire body is finely cast with detailed feathers. The details are believed to have been done with stamps carved with all the décor elements (similar to pattern blocks)<sup>[10]</sup>.



Fig. 3 — (a) This is part of a clay mold for casting a fang yi, around 1100 BC. Decorative plates could be interchanged within a mold to provide more variety [1]. (b) Fang-yi, Zhou dynasty, 11<sup>th</sup> century BC. Height is 35.6cm, width is 24.7cm, and weight is 9.92 kg. The Fang yi first appeared as a distinctive vessel type in the Shang dynasty and continued to be made into the early Spring and Autumn period (770-476 BC) [10].



Several industrial advances may also have encouraged rapid casting development, including progress in process planning, extracting, and refining. The evolution of foundry practices and the skills required for ceramics, mold making, metal refining, finishing, and machining all led to improved understanding and better castings. *Continued*



### Alloy variations

When compared with the consistency of European alloys, Chinese bronzes show huge variety. The percentage of tin could vary significantly, with other elements randomly included as well [4,9]. Throughout the Bronze Age in China, both binary (copper-tin or copper-lead) and ternary (copper-tin-lead) alloys are commonly found. Elemental analyses have been reported for a considerable number of bronzes with a provenance provided by archaeological documentation. The analyses show a wide range of compositions among objects from region to region, from a single site, even within a single tomb. This is not really surprising, even assuming an unrestricted supply of metals, since alloy composition is very difficult to control, and no ancient founder would have bothered to purify the metals and mix them in specific proportions.

For weapons, where mechanical properties are important, alloy control might have been attempted (though analytical data show little evidence of this). For vessels and statuary, however, all that was needed was an alloy that would cast well, and this was not a severe constraint. More important was the need to recycle the valuable bronze material; the founder who recycled miscellaneous artifacts (for instance, captured bronze weapons) sacrificed control of composition. It seems likely that the only control exercised came at the stage when the bronze was molten; if the

color or viscosity of

the molten metal did not seem right, the

founder added copper, tin, or lead to achieve a look that appeared consistent with previous melts [4].

### Color range

One reason for the prevalence of bronze may have been the color range that could be achieved by varying the alloy composition. For example, a polished bronze surface could take on a light pink hue, a light yellow tone, various shades of grey, or a copper-red shade, just by varying the percentage of copper, tin and lead. From the available evidence it appears that the ancient Chinese formulated their alloys, at least in some cases, with color in mind. The copper-tin-lead system exhibits a great range of physical properties that depend on composition as well; hardness varies with tin (and lead) content.

The most useful property of the copper-tin-lead system, however, is that it could be used for casting. The highest copper alloys (more than 97-98% copper) were difficult to cast due to high gas absorption and medium fluidity. The Chinese learned over time that tin acted as a deoxidizer, reducing gas absorption and promoting fluidity.

Alloys with more than 6 to 7% tin tended to cast well, and those with 10% tin or more were highly fluid with very good casting properties. Lead (up to 3%) increased the fluidity of the melt, and in any amount, lead improved the surface finish of the solidified casting [3]. For the most part, the alloys represented in a copper-tin-lead ternary phase diagram are not easily hot-worked or cold-worked in the solid state: They are difficult or impossible to shape by hammering.

However, alloys with high copper and low lead content, with tin less than 10%, can be hammered out to sheet, with frequent annealing. Bronzes with a tin content higher than 20%, and no lead, can be hot forged or quenched from a temperature above 550°C and cold-worked [3]. But if lead is present, these high tin bronzes are unworkable [3]. Over the whole field of the copper-tin-lead ternary phase diagram, lead in amounts more than 4% makes the alloy difficult to work. Some of the earlier artifacts from Gansu province are made of lead and copper alloys with very little tin. Lead persisted as an alloy constituent throughout the pre-Han period (Han period: 206BC-200AD).

### Casting methods

The ancient Chinese developed the piece mold process in which surfaces could be decorated by carving into the mold (for raised relief) or into the model (for recessed designs). A model of the item to be cast in bronze was sculpted out of clay and decorated with patterns and inscriptions. Early bronze vessels were cast with only one pour. Composite casting, a subgroup of piece mold casting, appeared during the Shang dynasty.

The technique was used to attach small appendages such as handles, to a larger vessel. Appendages were cast first, and then placed within the mold of the uncast larger vessel. Alloys were prepared in crucibles over a charcoal fire, and the molten material was then poured into the primary clay mold where it anchored the pieces in place [9]. The technique enabled the production of larger vessels and also facilitated the sculpting of many animated appendages.

During the Erligang period, when the foundries were greatly complicating mold making with elaborate decorations, many mold part assemblies were needed. From the scientific excavations at Anyang and later at Zhengzhou (both in Henan Province) where molds of grey fired clay were discovered, it was confirmed that the Shang used the direct casting (piece mold) method.

Large scale bronze metallurgy was seen at Erlitou in the Henan Province as early as 1500 BC [4]. Its bronze industry centered on the production of ritual vessels cast in clay section molds of two or more parts (Fig. 2-6) [4]. The bronzes found at



Fig. 5—This Si Yang Fang Zun, a bronze wine container with four rams, is an ambitious display of bronze casting technology. Ram heads emerge as three-dimensional sculptures, while their chests and front legs appear in relief amid a dense sea of spirals and scroll patterns. Incised birds with tall, scrolled crests cover the ram body. Three-dimensional snail-like horned dragons project outward from each side of the ram's head [13].

Sanxingdui looked dramatically different than the ritual vessels, yet were cast by the same techniques<sup>[4]</sup>. Heavy reliance on casting and on section mold casting in particular is a distinguishing characteristic for the bronze industry of the Erlitou, Erligang, and Sanxingdui cultures.

Chinese bronzes ornamented with ogres, dragons, and *taotie* beasts were distinguished by their disregard for realism in favor of bold exaggeration and distortion. The Chinese aristocracy had created a massive demand for such bronze ritual vessels with their religious and cultural ceremonies. The vessels also symbolized social status and power for the owner. The number and variety of vessel forms increased over time, and so did the complexity of decoration and manufacturing techniques. Developments of increasing sophistication occurred alongside improvements in casting technology. The evolution of foundry practices and the craftwork required for ceramics, mold making, metal refining, finishing and machining are responsible for the development of casting technology and the incredible discoveries that have been excavated.

**For more information:** Lisa Reiner is the Material Science and Corrosion Laboratories manager at California State University Northridge, College of Engineering, 18111 Nordhoff Street, Northridge, CA 91330-8332; tel: 818/677-7746; lisa.r.reiner@csun.edu; www.csun.edu/~mscl.

#### References

- [1] L. Ledderose, *Ten Thousand Things: Module and Mass Production in Chinese Art*, Princeton University Press, 2000.
- [2] W.T. Chase, "Bronze Casting in China: A Short Technical History," *The Great Bronze Age of China*, A Symposium, ed. George Kuwayama (Los Angeles County Museum of Art, 1983).
- [3] J. P. O'Neill, editor, Metropolitan Museum of Art, *Treasures from the Bronze Age of China: An Exhibition from the People's Republic of China*, New York: Metropolitan Museum of Art, 1980.
- [4] J. Xu, R. Bagley, editor, *Ancient Sichuan: Treasures from a Lost Civilization*, Seattle Art Museum, Princeton University Press, 2001
- [5] L. Yang and E. Capon, *Masks of Mystery: Ancient Chinese Bronzes from Sanxingdui*, Art Gallery of New South Wales, 2000.
- [6] S. Axton, "The Alchemy of Clay to Bronze," <http://www.cordair.com/axton/world.aspx>
- [7] X. Li, L. Ziming, R. W. Bagley and J. Xu, *Art of the Houma Foundry*, Princeton University Press, ©1996.
- [8] K. Y. Chen, *Brilliant and Affluent Bronzes of the Shang and Chou Dynasties*, National Museum of History Taipei, Editor, 1988.
- [9] R. Y. Lefebvre d' Argencé, M. H. De Young Memorial Museum: Ancient Chinese bronzes in the Avery Brundage Collection; a selection of vessels, weapons, bells, belthooks, mirrors, and various artifacts from the Shang to the Tang dynasty, including a group of gold and silver wares, Berkeley, Calif., Diablo Press, 1967.
- [10] S. D. Owyong, S. Hargrove and T. Lawton, *An-*



Fig. 6 — Si Mu Wu fang ding is a cooking vessel from the late Shang dynasty. Unearthed in 1939 in Anyang, it weighs 875 kg (1925 lb). An interior inscription is seen to the left, and decorative details are shown on the handle (right) [1]. This is the largest metal casting from Chinese antiquity. It is 133 cm (4.4 ft) high, 110 cm (3.6 ft) long, and 79 cm (2.6 ft) wide.

cient Chinese bronzes in the Saint Louis Art Museum, Publisher: St. Louis, Mo, 1997.

[11] J. A. Pope, R. J. Gettens, J. Cahill, N. Barnard, *The Freer Chinese Bronzes*, vol. 1, Catalogue, Washington, D.C., Smithsonian Institution, Freer Gallery of Art, 1967.

## CENTORR Vacuum Industries

Vacuum Hot Presses and Sintervac®  
for Ceramics and Metals



- Fires all non-oxides; SiC, Si<sub>3</sub>N<sub>4</sub>, AlN, BN, TiB<sub>2</sub>, and B<sub>4</sub>C; and metals.
- Pressings from 50 to 1500 ton
- Temperatures 1000-2500°C
- Diffusion bonding and powder compaction units available.

### Over 6000 units built since 1954

- Over 80 different styles of batch and continuous furnaces from 1 cu cm to 3 cu m
- Testing available in our Applied Technology Center furnaces to 2200°C.
- Worldwide Field Service and Spare Parts available for all furnace makes and models.

**Centorr Vacuum Industries, Inc.**

Ph: 603-595-7233 • Fax: 603-595-9220 • E-mail: sales@centorr.com

come see us at [www.centorr.com](http://www.centorr.com) for more details