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Implication of peritectic composition in historical high-tin bronze metallurgy

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ABSTRACT

Bronze alloys of varying tin contents from 0% to 28% were cast and then heated at elevated temperatures followed by quenching to examine the variation of microstructure, hardness and fracture characteristics. The results show that hardness increases with tin content and almost reaches the upper limit at 22% tin. Evidence has been found that the small-scale α dendrites spanning across the former β grains that were transformed to martensite serve as interlocking micro-bridges and thereby substantially reinforce the boundary strength to enhance fracture toughness. This effect is extremely sensitive to the α fraction and can best be obtained in alloys of near 22% tin. This specific composition, termed peritectic, seems optimal for sufficient strength without serious brittleness, and allows objects for a similar purpose to be made with less material. The choice of near peritectic composition in historical high-tin bronze metallurgy constitutes an excellent example of human adaptation to harsh environments where access to tin was limited and material cost had to be minimized.

1. Introduction

Archaeological evidence has it that, from within a few centuries after the first discovery of tin (Sn) alloying in copper (Cu) during the 4th millennium BC, the tin contents near 10% had long been perceived as a composition for the best mechanical property, i.e., strength without brittleness [1]. (The tin content in this article is based on weight fraction.) The Cu–Sn phase diagram in Fig. 1 [2] shows that this composition corresponds approximately to the upper limit to avoid formation of the δ phase in normal bronze casting, which is too brittle to accommodate impact loading either in fabrication or in use. Therefore the Cu–Sn alloys with tin content significantly above 10%, termed high-tin bronze, is fabricated primarily by casting to circumvent the problem arising from the brittle δ phase. High-tin bronze, with its lower melting points and better flow properties inside the mold, has long been used in the casting of bronze objects with complex shape or elaborate surface decoration, especially in ancient China where lead (Pb) was frequently added for further improvement of casting properties [3].

Surprisingly, high-tin alloys were often forged to produce some special bronze artifacts. Voce [4] may have been the first to report examples of forged high-tin bronzes in 1951. By examining microstructures of two Korean bronze bowls dated to the 12th to 14th century AD, he found the application of hot forging and quenching on alloys of about 20% tin. Further evidence was given on the use of a similar technology in Islamic Iran [5,6], Thailand [7,8], Central Asia [9,10], India [11], and Korea [12,13]. It is argued on archaeological evidence that this high-tin technology was practiced in India, Thailand, and Central Asia from as early as the 1st millennium BC. Goodway

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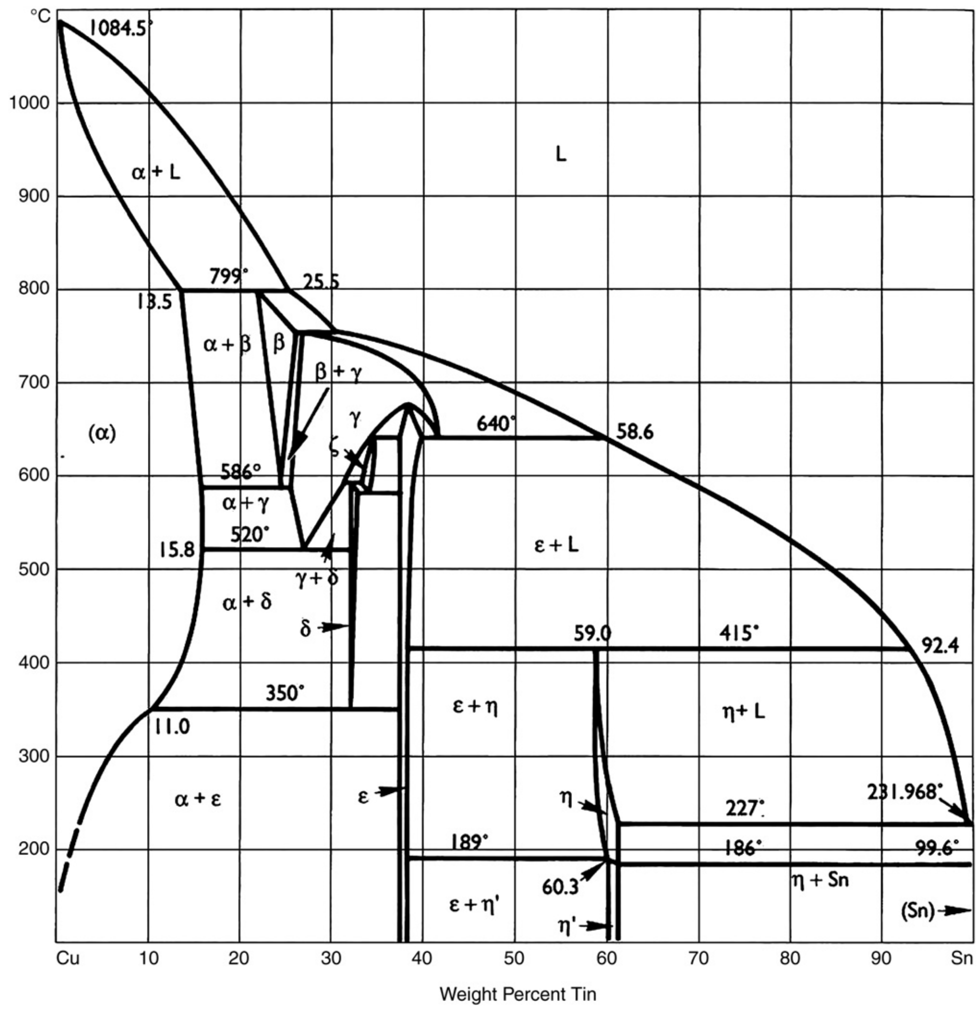

Fig. 1 – Cu–Sn phase diagram (quoted from "Meallography and microstructure of ancient and historic metals [2]).

and Conklin [14] and Sun and Wang [15] discussed the technical aspects of this technology applied in making musical instruments in the Philippines and in China. It is of significance that previous studies consistently reported high-tin bronze objects of near peritectic composition, 22% tin, shaped by forging and then finished by quenching from the $\alpha+\beta$ field of the Cu–Sn phase diagram. This technology of forging and quenching is in strong contrast to that of traditional China, based on casting and the ternary Cu–Sn–Pb alloys with substantial variation in alloy composition [3].

The consistency found in the forged high-tin bronzes that have been made in Korea for more than 1000 years suggests the presence of restrictions enforcing the selection of the specific tin contents and the associated thermo-mechanical treatments. Without doubt the increased tin content is beneficial in casting, but it can be detrimental to mechanical working unless the temperature is properly controlled, not to mention the disadvantage of high material cost due to the general tin shortage in pre-industrial Korea. Forging at the $\alpha+\beta$ phase field followed by quenching is then understood as an effort to keep away from the brittle δ phase in fabrication and use. This does not explain, however, the narrow range of compositions and temperatures consistently selected in preference. The equilibrium Cu–Sn phase diagram contains a wide range of other tin contents and temperatures that can suppress the δ formation and, at the same time, provide seemingly better material property or better economy. This study probes the implication behind the selection of peritectic composition in the high-tin bronze technology where the unique thermo-mechanical treatments of forging and quenching are necessary elements in fabrication. The Cu–Sn alloys with varying tin content were prepared and given thermal treatments for the control of microstructure. Hardness measurements were made on specimens with varying microstructure and their fracture characteristics were examined on polished surfaces as well as on fractured surfaces. The results were then compared with those obtained from examining bronze artifacts made in the Koryo (918–1392) and Choseon (1392–1910) dynasties of Korea [16].

2. Experiments

Alloys were made to the target compositions as specified in Table 1 using copper and tin ingots of commercial purities. The tin contents were chosen to cover the whole alloys that are