DEVELOPMENT OF LEAD FREE COPPER ALLOY GRAPHITE CASTINGS

Technical Report

by

P. K. Rohatgi

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ABSTRACT

Centrifugal casting of Copper alloys containing graphite particles established the feasibility of making hollow cylindrical castings. In these castings, the graphite particles are segregated to the inner periphery making them well suited for bearing applications because of the lubricity of the graphite particles. The recovery of graphite is found to be around 90%.

Chemical analysis shows that the average concentration of graphite particles near the inner periphery is 13 vol.% (3.5 wt.%) and 16.3 vol.% (4.54 wt.%) for castings made from melts originally containing 7 vol.% (2 wt.%) and 13 vol.% (3.5 wt.%) graphite particles, respectively. Hardness tests show that as the volume fraction of graphite particles increases, the hardness values in the graphite rich zone decreases. Also, it is found that as the volume fraction of graphite particles increases, the hardness values in the graphite rich zone is found to be widely scattered. The results indicate that it is feasible to centrifugally cast copper alloys containing dispersed graphite particles to produce cylindrical components with graphite rich inner periphery for bearing and plumbing applications.

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1. INTRODUCTION

This report summarizes the work undertaken by UWM Foundry and Composite Laboratories under DOE project entitled "Development of Lead-Free Copper Alloy-Graphite Castings." As a continuation of third year's work, centrifugal casting studies were pursued.

Centrifugal casting technique generates a graphite rich zone near the inner periphery of copper alloy containing graphite particles due to the lower density of graphite compared to the copper melt. For use as a bearing and cylindrical material or in plumbing applications where the hollow cylindrical geometry would be suitable, it is important to understand how the microstructure of graphite-rich zone of these composites depend on the synthesis parameters. During the past year, the effects of the rotational speed of the mold and the volume fraction of graphite particles on the porosity at the graphite rich zone were studied.

Samples were sent to three bearing industries (Glacier Clevite, Bunting Bearing, and Anni Mineral Processing) for testing. One company reported results showing that copper graphite alloys have better tribological properties compared to the currently used conventional copper bearing alloys containing lead.

2. SCOPE OF TASKS

In the third year of the program, primary efforts were directed towards characterization of the microstructure and properties of centrifugal castings.

3. EXPERIMENTAL PROCEDURE

C90300 copper alloy was melted in a graphite crucible using an induction furnace. Five micrometer graphite particles and the wetting agent were mixed into the copper alloy melt at 1150^{0}C using a vortex technique. The amount of graphite added to the melts were 2 wt.% (7 vol.%) and 3.5 wt.% (13 vol.%). These represent the quantities of graphite particles initially added to the melt. It is likely that some graphite was lost during mixing and the recoveries in the melt are slightly lower than the amounts added.

The graphite mold was inserted into the horizontal centrifugal casting machine and reheated using a burner. The molten copper alloy was poured into the horizontal centrifugal casting machine to cast cylindrical castings with an outer diameter of 9.5 cm, a wall thickness of 1.5 cm and a length of the casting of 13 cm. The speed of mold rotation was 800 rpm or 1900 rpm. Castings of C85500 alloy and C85500 alloy with 3.8 vol.% graphite were both made at 1900 rpm.

Multiple metallographic samples were taken from the centrifugally cast cylinders to observe the microstructures. Chemical analyses were performed, according to ASTM E 249 to evaluate the distribution of elements in the cross section of the centrifugal castings. The hardness across the cross section of the cylindrical castings was measured using the Rockwell hardness tester with 1/16 inch ball.

4. Results and Discussions

4.1 Microstructure analysis

Stir casting technique involves the addition of the graphite particles into the melt, followed by mixing of the slurry to obtain a proper shape of the casting. The fluidity of the melt which should be adequate to fill the mold depends on the melt temperature. Generally, the addition of solid particles into a melt is found to decrease its fluidity. Also, during mixing, the melt temperature decreases, leading to a further decrease in the fluidity. Therefore, after the addition of the particles into the melt, the proper melt temperature (which depends on the mixing time and the volume fraction of the particles added) is obtained by reheating the melt. However, the melt temperature cannot be increased arbitrarily to improve its fluidity, since above a certain temperature some loss of material by oxidation and evaporation would be extreme. The process of stir casting leads to flotation or settling of the solid particles in the during solidification due to the density differences between the particles and the melt.

Figure 1 shows the microstructure of centrifugally cast copper alloy to which originally 13 vol.% (3.5 wt.%) graphite particles were added, cast at 800 rpm. This figure shows that the movement of graphite particles to the inner periphery due to centrifugal forces forms three distinctive regions, (a) an essentially graphite free zone, (b) a transition zone and (c) a graphite rich zone at the inner periphery of the casting. This figure also shows that graphite particles are preferentially segregated in the interdendritic regions of both the graphite rich zone and the transition zone.

The segregation of the graphite particles near the inner periphery of the copper alloy castings was accompanied by a greater amount of the porosity compared to other regions (Figure 1c). The movement of graphite particles as well as bubbles of gas rejected by the solidifying copper alloy to the inner periphery during centrifugal casting is due to their lower density. In addition, the fluidity of the melt near the inner periphery of the centrifugal castings decreases due to the segregation of graphite particles, which restricts the movement of the porosity to the free surface.

Figure 2 presents the microstructure of centrifugally cast copper alloy containing 7 vol.% graphite particles, cast at 800 rpm, showing the concentration of the graphite particles at the inner periphery and porosity near the inner periphery, along with the segregation of the graphite particles in the interdendritic regions. Interestingly, the casting in Fig. 1, which originally contained 13 vol.% (3.5 wt.%) graphite contains more porosity at the inner periphery than the casting in Fig. 2, which originally contained 7 vol.% (2 wt.%) graphite.

Figure 3 shows the results of chemical analysis of the two copper alloy castings (originally containing 7 vol.% (2 wt.%) and 13 vol.% (3.5 wt.%) graphite particles) from the inner periphery to the boundary near the graphite-free zone. Figure 3 (a) made for the alloy containing 13 vol.% (3.5 wt.%) graphite particles, shows that the graphite particles are concentrated near the inner periphery to an average of 16.3 vol.% (4.54 wt.%). Fig. 3(b) made for the alloy containing 7 vol.% (2 wt.%) graphite particles, shows that the graphite concentration near the inner periphery is an average of 13 vol.% (3.5 wt%).

Figure 4 and Figure 5 shows the results of the X-ray analyses of the graphite-rich and graphite free-zones of the C90300 alloy containing 13 vol.% (3.5 wt%) graphite and

7 vol.% (2 wt.%) graphite, cast at 800 rpm. They indicate that the graphite particles are present in the graphite rich zone and the titanium added as a wetting agent, not surprisingly forms titanium carbide by reacting with the graphite. The titanium addition may form titanium carbide on the surface of graphite particles in the melt, reducing the contact angle between the graphite particle and the copper melt, facilitating the incorporation of the graphite particles into the copper melt. This would also increase the density of the graphite particle, leading to a decrease in the tendency of the graphite particles to float in the copper melt since the density of titanium carbide is 4.9 g/cm^3. Generally, if the density of the particle is lower than that of the melt, the holding of the melt after stir casting technique leads to the floatation of particles once the mixing is stopped.

Figure 6 shows the microstructure of the graphite rich zone of a copper alloy originally containing 7 vol.% (2 wt.%) graphite particles which was centrifugally cast at 1900 rpm. It shows the segregation of the graphite particles near the inner periphery and the concentration and agglomeration of graphite particles at the interdendrite region. Compared to Figure 2 for similar alloy cast at 800 rpm, the size of porosity seen in Figure 6 is larger. This suggests that the greater centrifugal force acting on the melt may help in moving the gas bubbles to the inner periphery and increase their size by coalescence of smaller bubbles into larger ones.

Figure 7 shows the microstructure at the graphite rich zone of centrifugally cast copper alloy containing 13 vol.% (3.5 wt.%) graphite particles, cast at 1900 rpm. Compared to Figure 1, this figure also shows that the size of porosity near the inner periphery of the centrifugal casting increases with increasing rotational speed. The high volume fraction of graphite particles near the inner periphery makes the movement of the porosity to the surface difficult. Chemical analysis and microstructural observations showed that the amount of graphite particles segregated near the inner periphery increases with an increase in the amount of graphite particles originally added to the melt 7 vol.% (2 wt.%) versus 13 vol.% (3.5 wt.%).

4.2 The thickness of graphite rich zone and the recovery of graphite particles

The thickness of the graphite rich zone is related to the distance traveled by the graphite particle in the melt in a given time before solidification and hindrance stops the movement of the particles. As the rotational speed increases, the travel distance increases due to a higher centrifugal forces applied to the particle. But, as the volume fraction of graphite particle increases, the distance traveled decreases due to an increase in the interaction between particles and hindrance each other. Table 1 shows the ratio of the thickness of the graphite rich zone to the thickness of the casting for copper alloys containing 7 vol.% (2 wt.%) and 13 vol.% (3.5 wt.%) graphite particles, cast at 800 rpm and 1900 rpm. This table shows that as the graphite volume percent increases and the rotational speed decreases the ratio of the thickness of the graphite rich zone to the casting thickness increases.

During the synthesis of metal matrix composites, the all of the particles added to the melt are not recovered in the castings. During mixing, pouring the molten copper melt containing graphite particles into the mold, some particles are lost. If the particles are not wetted by the melt, the loss increases. In this study, titanium is used as a wetting agent. The carbide formed on the surface of the graphite particle improves the wettability of the graphite by the copper melt. Also, the titanium carbide has a higher density (4.93 g/cm^3) than that of graphite (2.2 g/cm^3). Therefore the floatation velocity of the graphite particle in the copper melt is somewhat reduced. The degree of recovery of the graphite particles in centrifugal castings is calculated by dividing the volume fraction of graphite in the graphite rich zone of the centrifugal casting by the originally added graphite particles into the copper melt. That is;

$$\text{Recovery} = \frac{\varepsilon_p'}{\varepsilon_p}\left(\frac{\left(\frac{r_t}{r_0}\right)^2 - x^2}{1 - x^2}\right)$$

where ε_p is the volume fraction of the particles added initially into the melt and ε_p' is the volume fraction of graphite in the graphite rich zone, x is the ratio of the thickness of graphite rich zone to the total thickness, r_o is the total thickness of the casting, and r_t is the thickness of the graphite rich zone. ε_p' is estimated by measuring the average volume fraction of the particle in the graphite-rich zone. The recovery of the graphite particles is 97% and 95%, respectively, for the copper alloy castings to which originally 7 vol.% (2 wt.%) and 13 vol.% (3.5 wt.%) of graphite particles were added.

4.3 Hardness distribution of copper alloy castings containing graphite particles.

Figure 8 shows the hardness distribution across the cross section of centrifugal casting of C85500 alloy and C85500 alloy with 3.8 vol.% graphite, both cast at 1900 rpm. Figure 8(a) shows a uniform hardness (around HRF 90) across the wall thickness in monolithic alloy casting. The hardness in C85500 alloy containing graphite cast under similar conditions is shown in Figure 8(b). The graphite-free regions near outside diameter of the castings have hardness values exceeding HRF 90. Relatively lower values of hardness, below HRF 60, are observed in the graphite-rich region near the inner periphery of the casting. It should also be noted that the hardness of the copper alloy matrix in the graphite-free region of the alloy containing graphite seems to be somewhat higher than that of the centrifugally cast monolithic matrix alloy. This could be due to several factors, including differences in thermal conditions and cooling rates prevailing during casting of the alloys. The scatter of hardness values in the graphite rich regions (approx. 20 HRF) may be related to factors, such as the forced concentration and agglomeration of graphite particles in the copper melts during centrifugal casting, concentration of combined carbon (i.e., TiC), progressive freezing initiated from the mold wall, and porosity resulting from gas bubbles often attached to graphite particles.

Figure 9 shows the hardness distribution of C90300 alloy containing 7 vol.% (2 wt.%) and 13 vol.% (3.5 wt.%) graphite particles centrifugally cast at a speed of 1900 rpm. Compared to the hardness distribution of C90300 alloy containing 7 vol.% (2 wt.%) and 13 vol.% (3.5 wt.%) graphite particles centrifugally cast at a speed of 800 rpm, reported during the last year, this figure shows higher hardness values in the graphite-free regions. This may be due to the higher rotational speed of the mold, leading to an increase in the solidification rate.

4.4 Conclusions

1. 9.5 cm diameter cylindrical castings, were successfully made from copper alloys containing 7 vol.% (2 wt.%) and 13 vol.% (3.5 wt.%) graphite particles using centrifugal casting. Microstructural observations show that most of graphite particles

in the melt become concentrated near the inner periphery of the castings due to the lower density of the graphite particles compared to copper melts.

2. The porosity in the centrifugal castings is also concentrated near the inner periphery. The size of porosity near the inner periphery of casting increases with increasing volume fraction of the graphite particles and with the increasing rotational speed of the mold.

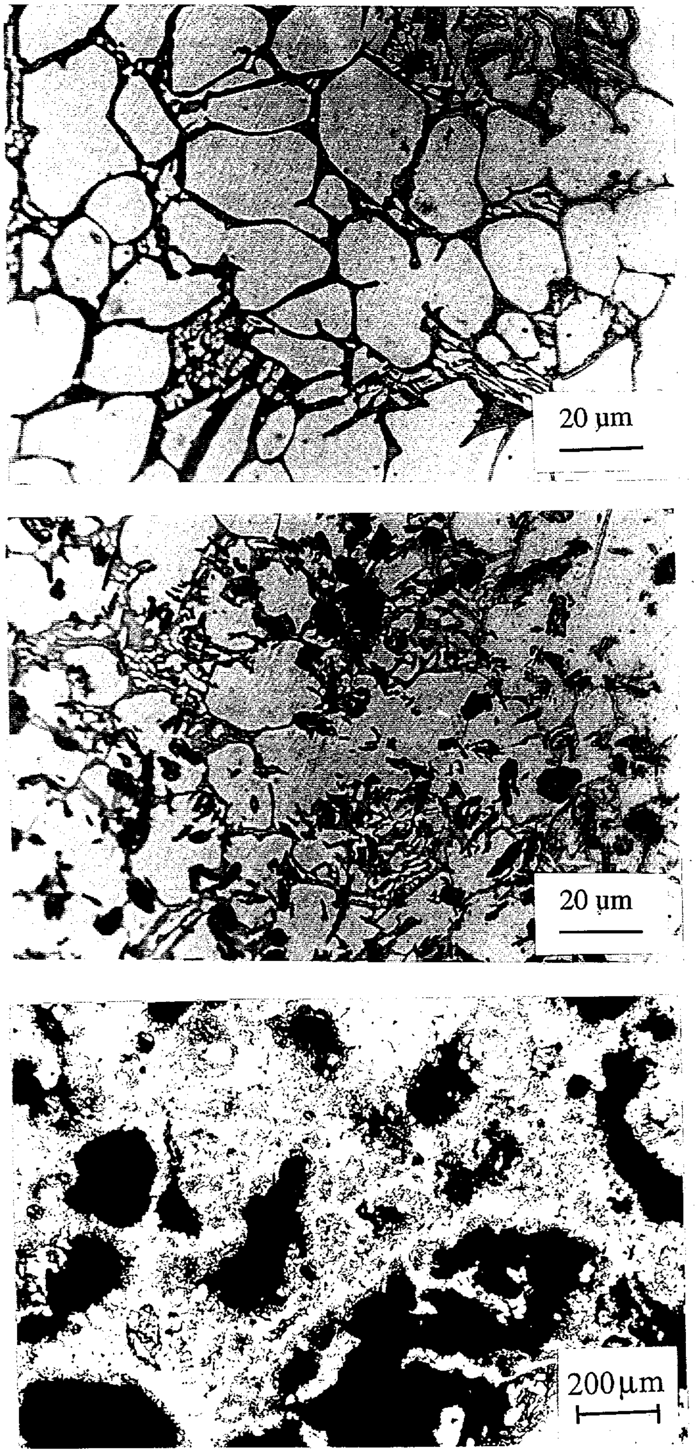
3. Chemical analysis of copper alloy melt originally containing 13 vol.% (3.5 wt.%) graphite, cast at 800 rpm, indicates that the average concentration of graphite particles near the inner periphery is 16.3 vol.% (4.54 wt.%). For the copper alloy originally containing 7 vol.% (2 wt.%) graphite particles, the content of graphite particles near the inner periphery is 13 vol.% (3.5 wt.%). These large volume percentages of graphite near the inner periphery will give improved tribological properties and machinability to copper alloys.

4. Average hardness of the graphite-free regions of centrifugal casting of copper alloy containing 13 vol.% (3.5 wt.%) graphite particles cast at 1900 rpm are higher than that observed in centrifugal castings of centrifugal casting of copper alloy containing 13 vol.% (3.5 wt.%) graphite particles cast at 1900 rpm. This may be due to an increase in the solidification rate. In the graphite-rich zone, the hardness values are relatively lower (20-40 HRF) compared to the hardness values in the graphite free zone (80-110 HRF). In addition the hardness values in graphite rich zones show a wide scatter. A wider scatter has been attributed to graphite agglomeration and the associated porosity.

5. The results indicate that it is feasible to produce cylindrical components with graphite rich zone near the inner periphery by centrifugally casting lead free copper alloy melts containing suspended graphite particles. These cylindrical castings will be eminently suitable for lead free bearing and plumbing applications.

Table 1. Ratio of the thickness of the graphite-rich zone to the total thickness of the casting (x)

Graphite (v/o)	Rotational Speed rpm	X
7	800 1900	0.56 0.42
13	800 1900	0.76 0.71



A

B

C

Fig. 1. Microstructure near the inner periphery of centrifugally cast copper alloy containing 13 vol.% graphite particles, cast at 800 rpm. (a) graphite-free zone, (b) transition zone, (c) graphite-rich zone.

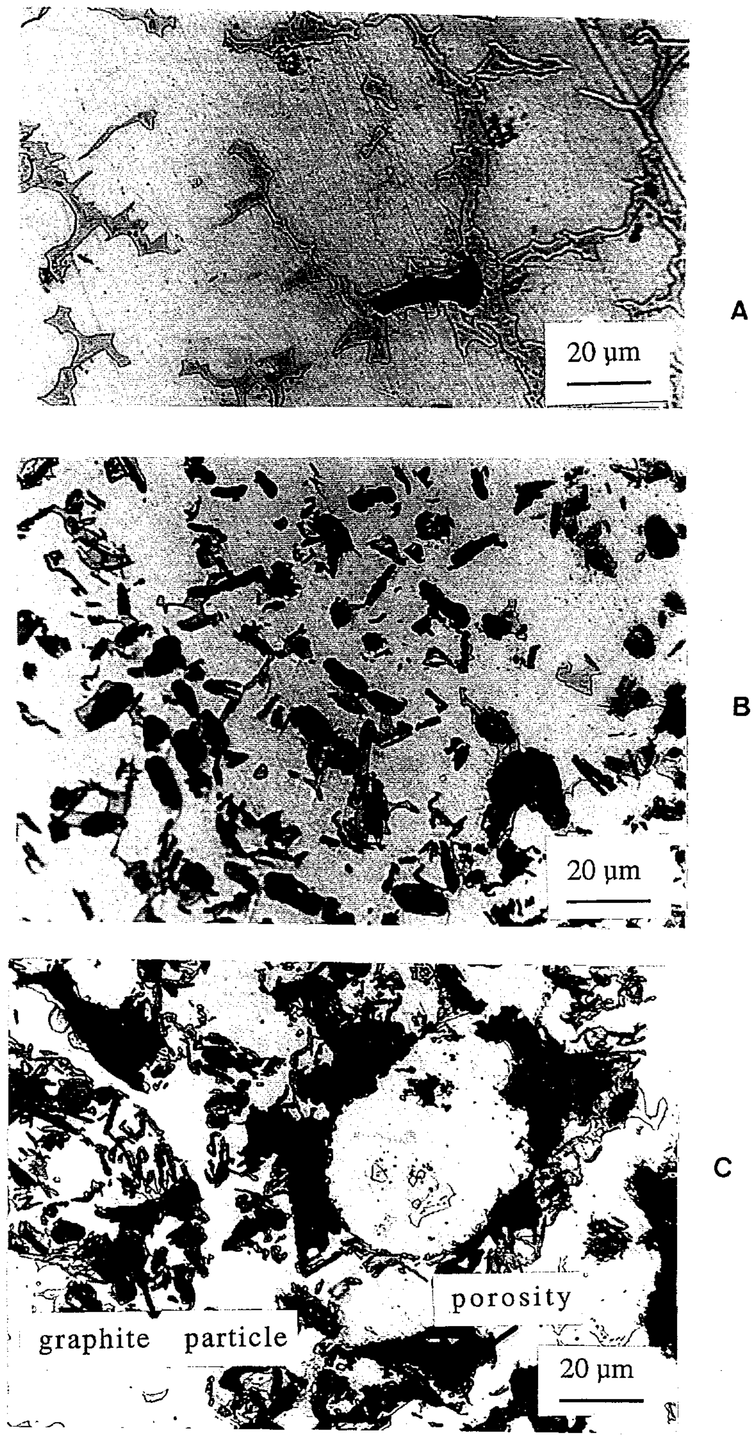
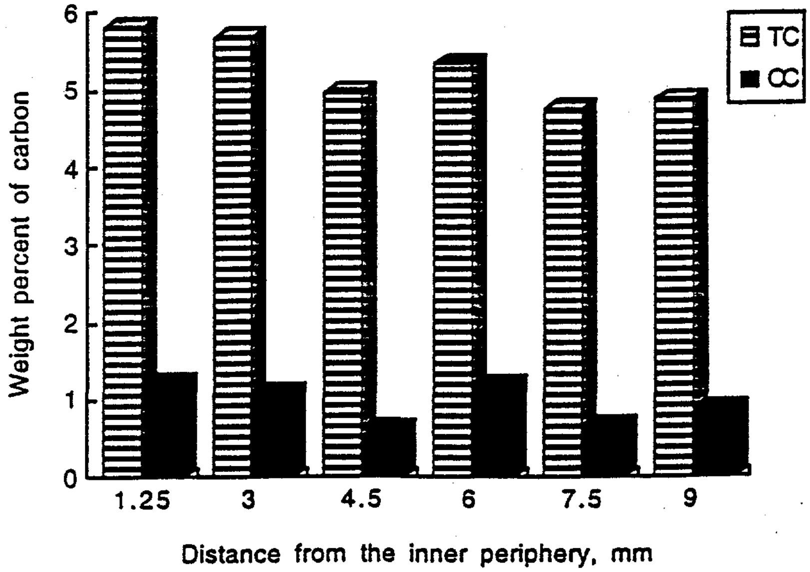
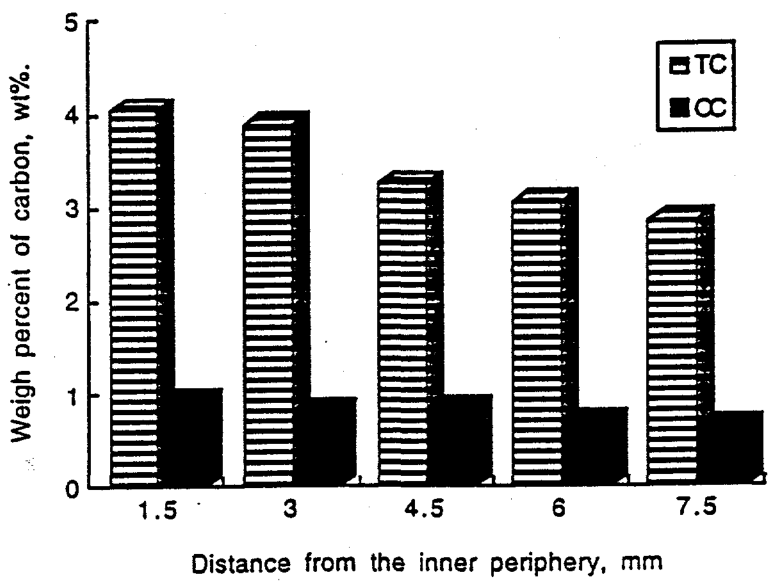


Fig. 2. Microstructure near the inner periphery of centrifugally cast copper alloy containing 7 vol.% graphite particles, cast at 800 rpm. (a) graphite-free zone, (b) transition zone, (c) graphite-rich zone.

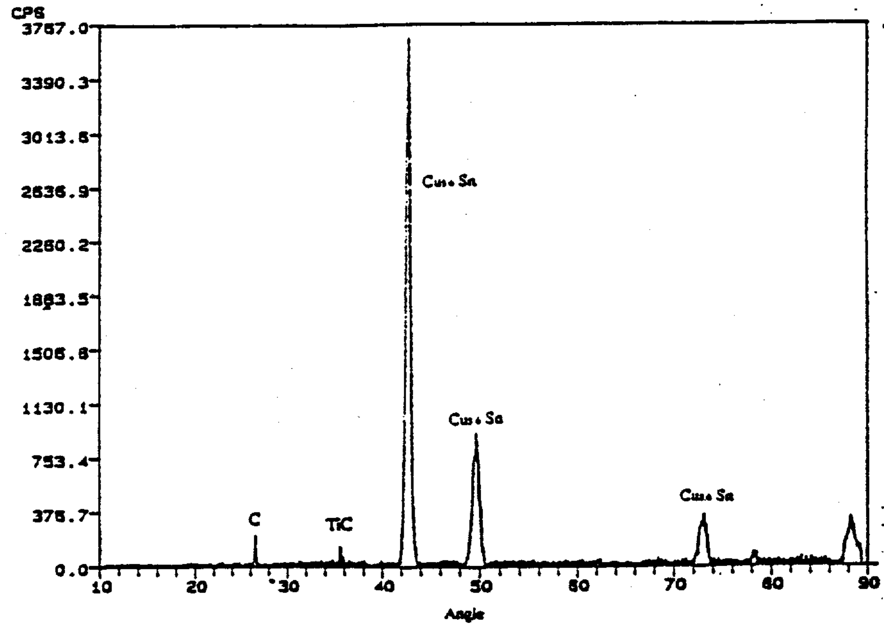


(a)

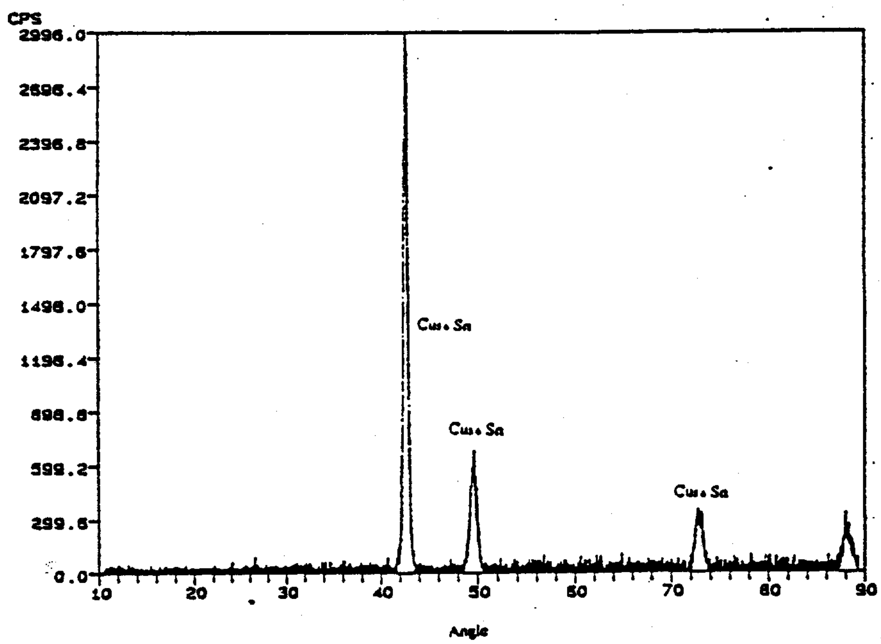


(b)

Fig. 3. Distribution of graphite particles in centrifugal casting of C90300 alloy containing (a) 13 vol.% and (b) 7 vol.% graphite, cast at 800 rpm. (TC: total Carbon, CC: combined Carbon)

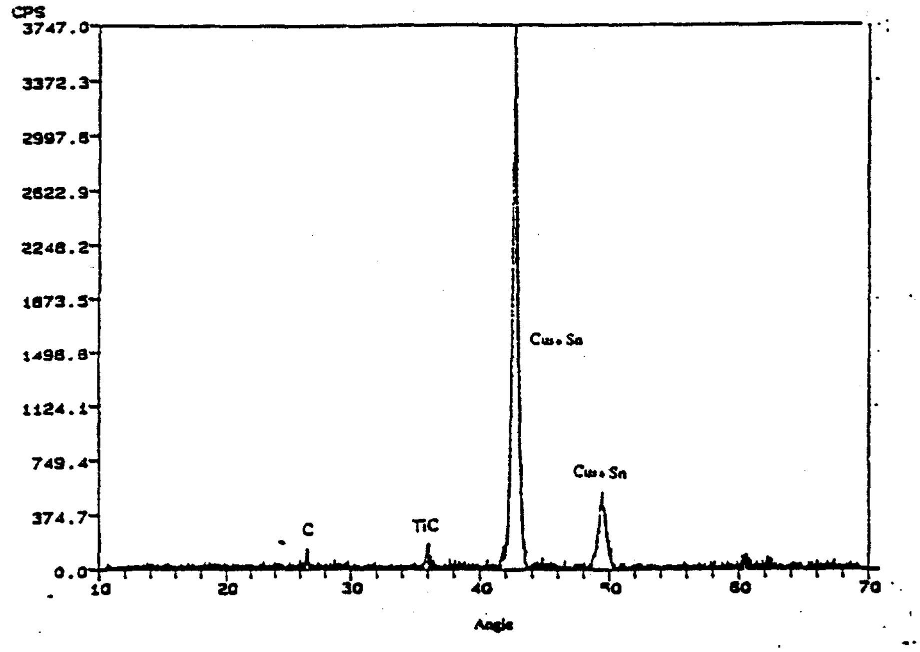


(a)

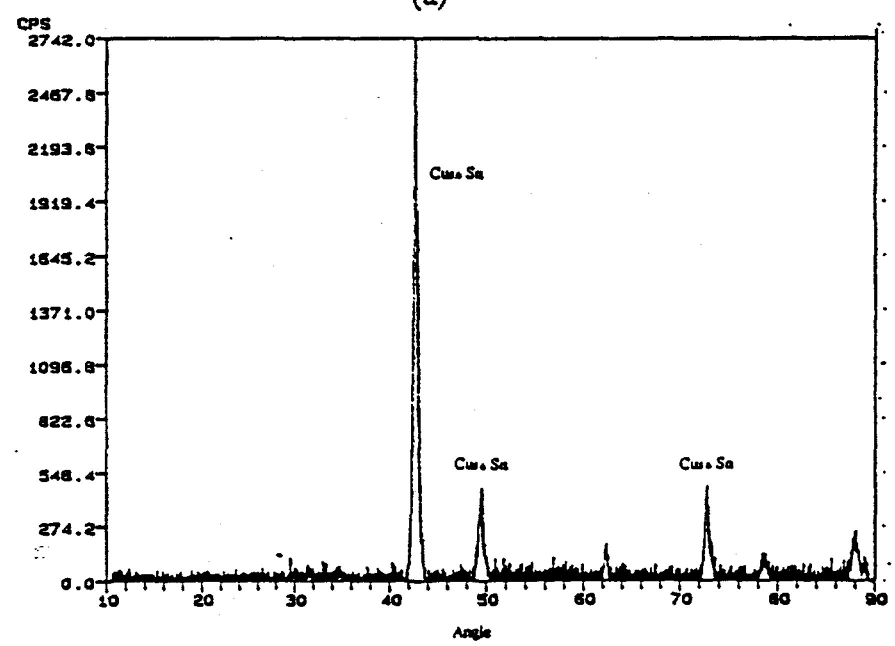


(b)

Fig. 4. X-ray analysis of (a) the graphite-rich zone and (b) the graphite-free zone of C90300 alloy containing 13 vol.%, cast at 800 rpm.



(a)



(b)

Fig. 5. X-ray analysis of (a) the graphite-rich zone and (b) the graphite-free zone of C90300 alloy containing 7 vol.%, cast at 800 rpm.

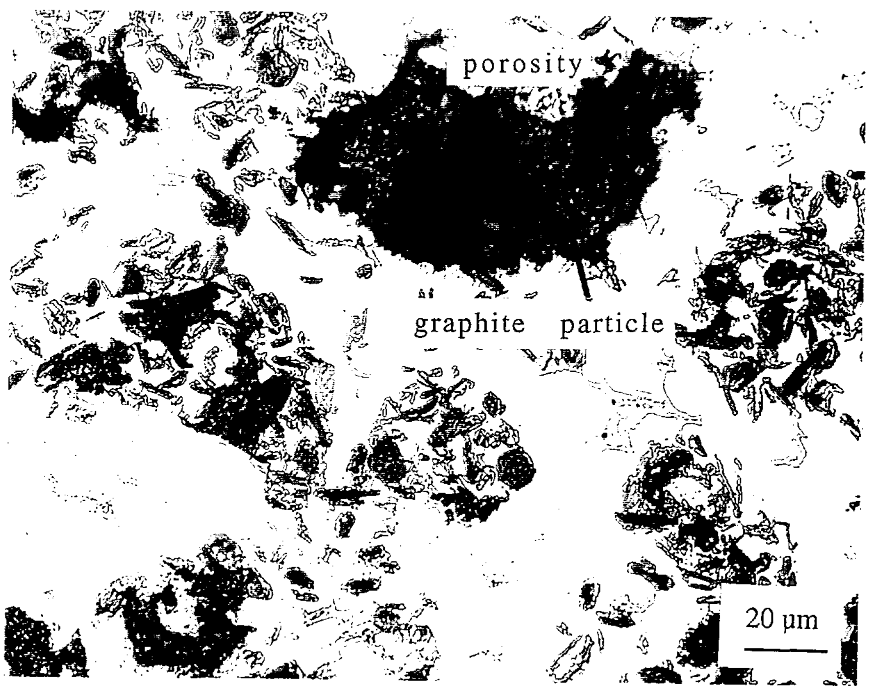


Fig. 6. Microstructure near the inner periphery of centrifugally cast copper alloy containing 7 vol.% graphite particles, cast at 1900 rpm.

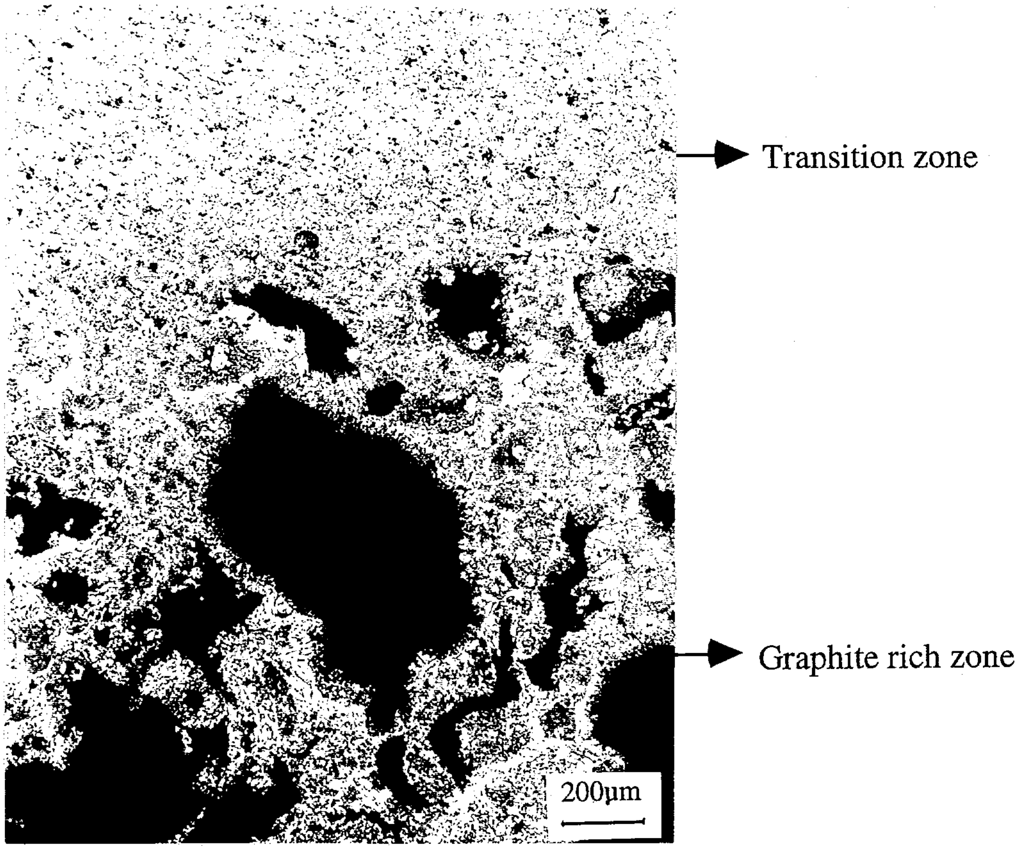
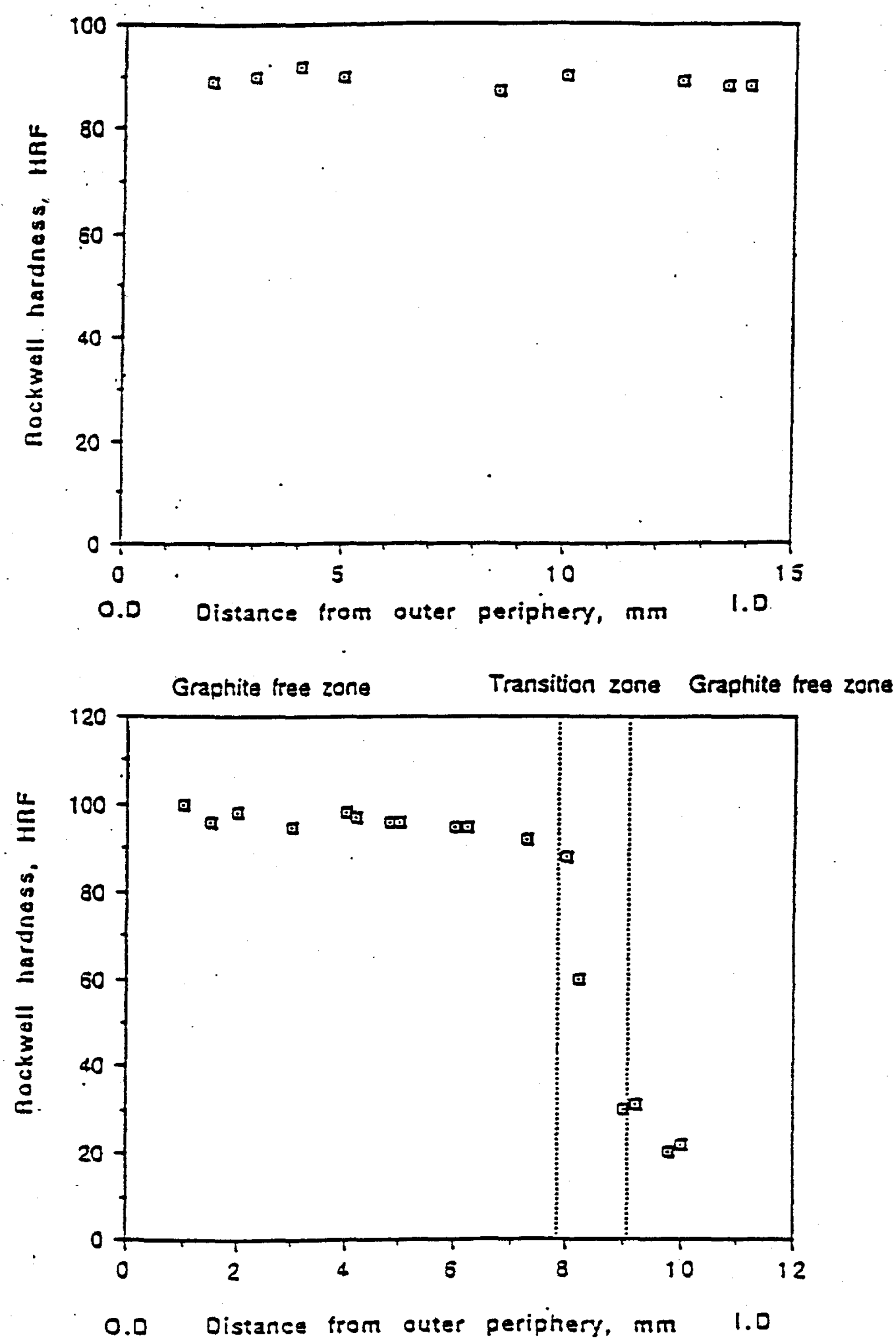


Fig. 7. Microstructure near the inner periphery of centrifugally cast copper alloy containing 13 vol.% graphite particles, cast at 1900 rpm.



(a)

(b)

Fig. 8. Hardness distribution in the cross section of centrifugal casting of a) C85500 alloy, and b) C85500 alloy with 3.8 vol.% graphite, both cast at 1900 rpm.

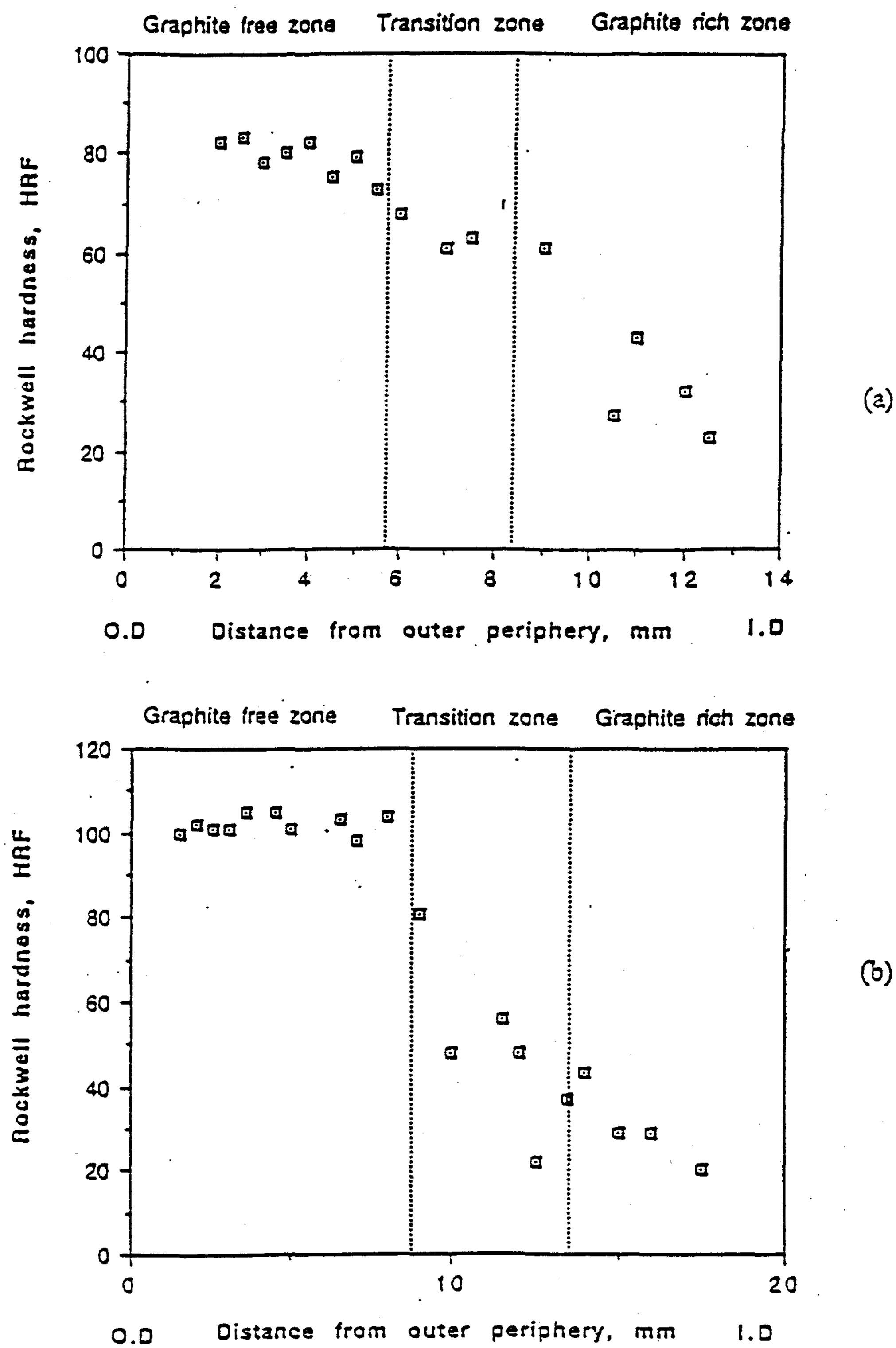


Fig. 9. Hardness distribution in a cross the longitudinal section of centrifugal casting of (a) C90300 alloy containing 7 vol.% graphite and, (b) C90300 alloy containing 13 vol.% graphite, both cast at 1900 rpm.