Microstructure and Properties of Lead-Free Free-Cutting Graphite Brass Prepared by Cementite Graphitization (Postprint)

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Abstract

Eutectic cast iron (ECI) was used as a carbon source to prepare graphite brass through in-situ cementite formation during melting and casting, followed by a cementite graphitization process. The microstructure of the graphite brass was analyzed using SEM and EDS, and the relationship between microstructure, mechanical properties, and machinability was investigated. The results show that the in-situ formed cementite decomposes into graphite particles after graphitization annealing, which are uniformly dispersed in the brass matrix with particle sizes of 3-6 m; graphite particle segregation occurs when the cast iron addition reaches 7%. With increasing cast iron addition, the matrix structure is continuously refined, tensile strength and microhardness increase, while elongation decreases; with increasing graphite volume fraction, the chip morphology of the graphite brass continuously improves. At a cast iron addition of 5%, the brass exhibits the best chip morphology, consisting of short flake-like and C-type chips, and its machinability is comparable to that of leaded brass HPb59-1.

Full Text

Microstructures and Properties of Lead-Free Free-Cutting Graphite-Brass Prepared by Graphitization of Cementite

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Abstract

Graphite is believed to be an attractive candidate substituting for lead to produce free-cutting brasses, because of its lubricating property and the role in chip breaking. The major hindrances of developing graphite-brass are the large density difference and nonwetting characteristic between graphite and copper. In this work, eutectic cast iron (ECI) was added into brasses instead of other form of carbon source. Cementite particles were in situ formed during casting, then annealing treatment was conducted to facilitate the graphitization of cementite particles, and finally uniformly dispersed graphite particles with the size of 3~6 mm were obtained in brass alloys. SEM and EDS observation indicate that the microstructures of the graphite-brass are refined with the cast iron content increased from 1% to 7%. The tensile strength and microhardness are increased, and the chip morphologies are improved gradually with the cast iron content increased from 1% to 7%. However, the graphite brass with 7% addition shows suboptimal chip morphologies because of the segregation of graphite particles. The chips of graphite brasses with 5% addition are desired, which are short and discontinuous. Its tensile strength, elongation and Vickers hardness are 502.00 MPa, 22.6% and 148.9 HV, respectively. The graphite brass shows comparable machinability to conventional lead brass HPb59-1.

KEY WORDS graphite-brass, graphitization of cementite, microstructure, machinability

Introduction

Lead brass exhibits excellent machinability and mechanical properties, and is widely used in bearing and free-cutting tool manufacturing due to its low cost. However, the inherent water-soluble Pb leaching from lead brass severely pollutes the environment and damages human health, making the development of lead-free free-cutting brass an imperative challenge. Current design strategies for lead-free free-cutting brass involve adding brittle particles similar to Pb, which can be either elemental or compound phases. Elemental brittle particles primarily include lead-like elements (such as Bi, Sb, Te, etc.), which are essentially insoluble in Cu and exist in a dispersed state within the brass matrix. The chip-breaking effect and lubrication provided by these particles improve machinability, with bismuth brass being the most maturely studied system. Nevertheless, bismuth-induced grain boundary embrittlement severely compromises mechanical properties, and the scarcity of lead-like elements limits widespread application of these alloys.

Silicon brass utilizes brittle Si-rich compounds to generate chip-breaking effects for improved machinability, but these compounds lack the lubricating characteristics of Pb, resulting in a performance gap compared to lead brass. Moreover, the Cu content in silicon brass is significantly higher than in lead brass (Si has a Zn equivalent value as high as 10, limiting Zn content), which substantially increases alloy costs. Evidently, developing a lead-free free-cutting brass that can truly replace lead brass remains a considerable challenge.

Graphite brass has long been considered the most promising candidate to replace lead brass because graphite exists as brittle, soft particles in the brass matrix, similar to Pb, and serves as an excellent solid lubricant, producing both chip-breaking and lubricating effects analogous to Pb particles. However, the poor wettability and large density difference between graphite and copper make it difficult to generate uniformly distributed fine graphite particles in the brass matrix. To address these issues, Nath et al. prepared graphite brass using a combination of stir casting and extrusion; Kim et al. employed centrifugal casting; and Imai et al. utilized high-energy ball milling to uniformly mix Cu and graphite powders followed by spark plasma sintering. However, the machinability of these graphite brasses still lags behind lead brass because these methods fail to fundamentally solve the problem of extremely low carbon solubility in molten brass. Consequently, graphite exists not as a dispersed phase but as clustered flocculent aggregates at grain boundaries.

To enhance carbon solubility in molten brass, Rohatgi et al. added Ti and used stir casting, while Huang Jinsong et al. added Si and Mg. Although Ti and Si can increase carbon solubility to some extent, they simultaneously generate hard carbide particles, leaving a performance gap for practical applications. Therefore, the key to preparing graphite brass with excellent machinability lies in developing a method that can increase carbon solubility in molten brass without forming hard carbide particles in the matrix.

This work aims to develop high-performance graphite brass and demonstrates that adding cast iron instead of direct graphite addition can achieve the desired effect while improving wettability between graphite and the Cu matrix, thereby enhancing machinability. By analyzing the mechanical properties and machinability of graphite brass prepared with different cast iron additions, this study investigates the influence 规律 of varying cast iron content on the microstructure and properties of graphite brass.

Experimental

High-purity electrolytic Cu (>99.9%), pure Zn (>99.9%), and eutectic cast iron (4.3 wt% C) were used as raw materials. Alloys were prepared with 1%, 3%, 5%, and 7% eutectic cast iron additions (corresponding to graphite volume fractions of 0.2%, 0.6%, 1.1%, and 1.5%, respectively). The alloy materials were melted in a medium-frequency induction furnace and cast into 70 mm diameter rods in an iron mold. The cast rods were heated to 750 °C and extruded into 20 mm diameter round bars using a 300 t vertical extrusion machine with an extrusion ratio of 12. Subsequent graphitization annealing was performed at 850 °C for

4 h in H_2 atmosphere, during which cementite fully graphitized to produce the desired graphite brass.

Microstructural observation and EDS analysis were conducted using a Quanta 200F scanning electron microscope (SEM) and Microlab MK II energy dispersive spectrometer (EDS). SEM samples were prepared by grinding, polishing, and etching with a solution of 30 mL $K_2Cr_2O_7$ + 6 mL H_2SO_4. The volume fraction of particles was analyzed using Image-Pro Plus software. Particle size was determined by the linear intercept method (ASTM E 122-96) through statistical analysis of no fewer than 300 dispersed particles, followed by particle size distribution plotting. Hardness testing was performed on an HV-1000 microhardness tester with a 100 g load and 15 s dwell time; five measurements were taken for each sample and averaged. Tensile testing at room temperature was conducted on a CSS-44200 universal electronic testing machine using plate specimens prepared according to GB/T 228-2002 with a gauge length of 100 mm and crosshead speed of 1 mm/min. Turning tests were performed on a CW6136 horizontal lathe using W18Cr4V high-speed tool steel without cutting fluid at a spindle speed of 570 r/min, feed rate of 0.08 mm, and cutting depth of 0.5–0.8 mm. Machinability was evaluated by analyzing chip morphology and size during cutting.

2.1 Microstructural Analysis

[Figure 1: see original paper] shows SEM images of as-cast and annealed brass with 5% cast iron addition, along with EDS spectra. Both as-cast and annealed brass exhibit $\alpha+\beta$ dual-phase microstructures with fine second-phase particles distributed in the matrix. During casting, the rapid cooling rate prevented complete $\beta\rightarrow\alpha$ transformation and α phase growth, resulting in a matrix consisting primarily of β phase with fine α phase (Fig. 1a). After annealing at 850 °C, the $\beta\rightarrow\alpha$ transformation proceeded fully during slow furnace cooling, causing the α phase to coarsen and increase significantly in volume fraction compared to the as-cast condition (Fig. 1b). Particle size was approximately 2 m in the as-cast brass with a spacing of about 10 m, while annealed brass showed particles of about 4 m with spacing of approximately 8 m.

EDS analysis identified the phase composition. Spectra from the as-cast brass matrix and dispersed particles (Figs. 1c and d) reveal that the dispersed particles are cementite containing approximately 2.4 wt% Fe dissolved in the matrix. After annealing, the matrix Fe content increased to 4.8 wt%, while the dispersed particles contained only carbon with no detectable Fe (Figs. 1e and f). This indicates that nearly all cementite particles transformed to graphite particles during graphitization annealing, with a graphite volume fraction of about 1.1%, consistent with theoretical values. Defects generated during extrusion facilitated Fe diffusion, accelerating cementite decomposition and promoting graphitization.

[Figure 2: see original paper] schematically illustrates the in-situ cementite formation during solidification and the subsequent graphitization annealing process.

During solidification, carbon first crystallizes from the Cu-Zn-Fe-C melt under the influence of undercooling. The carbon phase formation is governed by combined thermodynamic and kinetic factors. Kinetically, the difference in carbon content between cementite (6.69 wt%) and the melt (0.2 wt%) is much smaller than that between graphite (100%) and the melt, and the short-range ordered atomic clusters in the melt structurally resemble cementite. Thus, cementite formation is favored over graphite both compositionally and structurally. Thermodynamically, however, graphite is the stable phase with lower free energy than metastable cementite, giving graphite formation an energetic advantage. Slow cooling (e.g., furnace cooling) promotes graphite formation, but due to its low density and poor wettability with the melt, graphite particles float to the surface, resulting in extremely low carbon content in the brass and severe Fe segregation. Rapid cooling (e.g., casting into an iron mold) causes carbon to precipitate as in-situ cementite particles, which serve as nucleation cores that significantly increase nucleation rate and accelerate heterogeneous nucleation. The final carbon content after solidification shows minimal reduction from the initial addition, with Fe uniformly distributed in the matrix. The rapid cooling also limits $\beta \rightarrow \alpha$ transformation, yielding a microstructure of β phase, Fe_3C, and minor α phase.

During annealing, cementite graphitization involves cementite decomposition and Fe atom diffusion from cementite into the brass matrix. Since carbon has extremely low solubility and diffusivity in the brass matrix, each cementite particle transforms into a graphite particle, making graphite size dependent on cementite size. The graphite particles are larger than the original cementite particles (Figs. 1a and b) because graphitization is a volume-expansion process. Consequently, graphite particle positions remain unchanged while sizes increase slightly during annealing. Simultaneously, annealing promotes α phase precipitation and growth from the β phase, with slow cooling allowing substantial α phase coarsening and leaving only minor residual β phase. The final annealed microstructure consists of α phase, graphite, and minor β phase, consistent with Fig. 1b.

[Figure 3: see original paper] presents SEM images of annealed graphite brass with 1%, 3%, 5%, and 7% cast iron additions. All specimens exhibit $\alpha+\beta$ microstructures with minor β phase distributed in the α phase matrix. Dark cavities dispersed in the matrix result from second-phase particle pull-out during polishing. EDS analysis confirms these second-phase particles are graphite. At low cast iron additions, the matrix structure is coarse with few, sparsely distributed graphite particles (Fig. 3a). As cast iron content increases, the matrix becomes finer and more uniform, graphite particles increase in number and decrease in spacing, and distribution becomes more uniform and dispersed (Figs. 3b and c). However, at 7% addition, obvious graphite particle segregation occurs (Fig. 3d).

The graphite particle size distributions in annealed graphite brass with different cast iron additions are shown in [Figure 4: see original paper]. All distributions exhibit single normal distributions, with particle size decreasing as cast iron addition increases. The average graphite particle sizes are 5.86, 4.42, 4.02, and 3.57 m for 1%, 3%, 5%, and 7% additions, respectively. At 5% addition, particle size remains around 4 m with optimal size uniformity and dispersion.

The microstructural refinement and increased graphite particle count with higher cast iron additions result from the dependence of graphite size and position on cementite particles, whose nucleation and growth are influenced by cooling rate and cast iron content during solidification. Cementite preferentially nucleates in the melt under high cooling rates. According to the Johnson-Mehl-Avrami equation, undercooling affects both nucleation rate and growth rate, which increase with undercooling, but nucleation rate increases more rapidly. Therefore, under rapid cooling conditions, increasing cast iron addition raises cementite nucleus density, facilitating crystallization and yielding finer matrix structures and cementite particles, which translates to smaller graphite particles after annealing. The graphite particle segregation at 7% addition relates to the low Fe solubility in brass; when Fe reaches saturation solubility, phase separation occurs in the liquid to form Fe-rich regions and compositional segregation, consistent with literature reports.

2.2 Mechanical Properties

The mechanical properties of graphite brass with different cast iron additions and lead brass HPb59-1 are listed in . Tensile strength, yield strength, and microhardness increase with cast iron addition, with properties equivalent to or better than lead brass HPb59-1. Although graphite particles reduce brass hardness, the solid solution strengthening from Fe and grain refinement effects are more pronounced, leading to continuous increases in strength and hardness with cast iron content. However, elongation decreases because the extremely low toughness and strength of graphite particles act as microcracks in the high-strength brass matrix; more graphite particles create more microcracks, making the material more susceptible to fracture and reducing ductility.

Mechanical properties partially reflect machinability. Higher hardness increases cutting forces and tool wear while degrading surface quality, whereas higher ductility makes chip breaking difficult and causes severe built-up edge, increasing surface roughness. Optimal machinability requires balanced ductility, strength, and hardness. Literature indicates that materials with tensile strength of 441–558 MPa, elongation around 20%, and Brinell hardness of 100–150 HB are considered free-cutting. Compared with HPb59-1 properties, graphite brass with 3% and 5% cast iron additions exhibits similar mechanical properties within the free-cutting range.

2.3 Machinability Analysis

Chip morphologies of graphite brass with 1%, 3%, 5%, and 7% cast iron additions are shown in [Figure 5: see original paper]. At 1% and 3% additions, chips exhibit continuous spiral morphologies, though chips from the 3% alloy are relatively finer. The 5% addition produces short flake and short C-type chips with high surface finish quality. The 7% addition yields short spiral and C-type chips that are finer and more uniform than the 3% alloy but longer and larger than the 5% alloy. The dispersed graphite particles, being soft and brittle, facilitate microcrack initiation at the cutting edge during machining. These cracks propagate with tool advancement, producing chip-breaking effects similar to Pb particles.

Chip morphology demonstrates that graphite particles generated from cast iron addition significantly improve machinability, with chip morphology improving as graphite volume fraction increases. The optimal machinability occurs at 5% cast iron addition. Although the 7% addition contains higher graphite content, particle segregation (Fig. 3d) leads to non-uniform chip morphologies with spiral and C-type shapes, resulting in inferior machinability compared to the 5% alloy. Additionally, as an excellent lubricant, graphite forms a thin film between the tool and workpiece surface during cutting, reducing friction and producing smooth surfaces. Therefore, the optimal cast iron addition is 5%, yielding machinability comparable to lead brass HPb59-1.

Conclusions

(1) Graphite brass was successfully prepared using eutectic cast iron as the carbon source through melting-casting, hot extrusion, and graphitization annealing. The graphite brass exhibits a typical α+β dual-phase structure with graphite particles (3-6 m) dispersed in the brass matrix. As cast iron addition increases, graphite volume fraction increases while particle size decreases, and the matrix structure becomes finer and more uniform. Graphite particle segregation occurs at 7% cast iron addition.

(2) Tensile strength and microhardness of graphite brass increase with cast iron addition, while elongation decreases. Chip morphology improves with increasing graphite volume fraction. The optimal chip morphology—short flakes and short C-types—occurs at 5% cast iron addition, with tensile strength of 502.00 MPa, elongation of 19.2%, and microhardness of 148.9 HV. At this composition, graphite brass achieves optimal mechanical and machining properties comparable to lead brass HPb59-1.

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Note: Figure translations are in progress. See original paper for figures.