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New High-Temperature Copper Alloys

A. Popa, S. Constantinescu, J.R. Groza, and I. Bock

New high-strength, high-temperature Cu-Ni-Si alloys have been developed using additions of Cr, Zr, and/or Ti. These new alloys remain as precipitation hardenable as the base alloy, but the main strengthening phase may be different than Ni_2Si (e.g., Cr_2Ti). Substantial increases in mechanical strength were observed at both room and high temperature (773 K) when additions of Cr+Zr+Ti and Cr+Zr were made. Industrial testing of these alloys indicated a sevenfold increase in the lifetime of lateral blocks in continuous casting equipment of copper alloys.

Keywords

copper alloys, Cu-Ni-Si-Cr-Zr-Ti alloys, fractography, fracture toughness, tensile testing

1. Introduction

THE MAIN attraction of copper alloys is the combination of high mechanical strength and high thermal conductivity at room and elevated temperatures. For moderate temperature ranges (up to 673-773 K), a high mechanical strength can be achieved by using precipitation-aged copper alloys, such as Cu-Cr, Cu-Zr, Cu-Cr-Si, or Cu-Ni-Si. The strengthening is provided by the precipitation of the hard secondary phases, which are not soluble in the copper matrix at lower temperatures. This lack of solubility is critical for retaining the high thermal conductivity of the pure copper matrix after the precipitation of excess solute, such as Cr or Zr. This concept equally applies to ternary alloys (e.g., Cu-Ni-Si), in which the ratio of the two solutes is selected such that only an intermediate compound is formed, leaving no solute to dissolve in the copper matrix. For instance, an Ni:Si ratio of 2:1 or a Cr:Si ratio of 3:1 are selected such that all solutes combine to form Ni_2Si or Cr_3Si, respectively. Furthermore, copper-base alloys exhibit good room- and high-temperature formability, thus permitting a wide combination of mechanical strength, ductility, and thermal conductivity obtained by thermomechanical processing.

The benefits of using such high-temperature, high-strength Cu-base alloys for molding tools are derived from providing a higher and more uniform cooling rate, better fabricability, shorter cycle times, and thus higher productivity. For instance, Cu-Ni-Si bronze molds yield a 50% increase in casting rate and 5 to 8 times longer life as compared to a nitrided refractory steel mold (Ref 1, 2). However, there are some concerns about the durability of such copper alloy molds. To increase durability, Cr, Zr, and/or Ti were added to Cu-Ni-Si. All these additions are known to increase refractory and mechanical properties without considerably affecting the heat conductivity of Cu. The objective of the present work was to understand this unusual high-temperature behavior and define the predominant microstructural features responsible for retaining the high-temperature strength in the new quaternary or complex Cu-Ni-Si alloys.

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2. Experimental Procedure

2.1 *Materials*

The materials used in the present investigation were Cu-Ni-Si alloys with Cr, Zr, and/or Ti additions (Table 1). In most cases, the Cu-Ni-Si baseline alloy was approximately Cu-4at.%Ni-2at.%Si (3.75wt%Ni-0.90wt%Si). The alloys were prepared by induction melting and mold casting. Cast specimens were homogenized, hot rolled, solutionized, quenched, and aged in different conditions.

Table 1 Chemistry and mechanical properties of Cu-Ni-Si alloys with Cr, Zr, and Ti additions

Alloy	Additions, wt%			UTS, MPa		Yield strength, MPa		HB,
	Cr	Zr	Ti	20°C	500 °C	20 °C	500 °C	20 °C
1	...	...	...	581	209	337	186	239
2	0.22	...	...	452	255	390	217	202
3	0.6	...	...	440	216	311	195	197
4	0.2	0.01	...	545	286	450	205	218
5	0.41	0.02	...	516	281	395	200	201
6	0.54	...	0.05	461	281	360	202	194
7	0.58	...	0.27	477	236	352	192	180
8	0.36	0.02	0.01	625	327	526	295	216

UTS, ultimate tensile strength

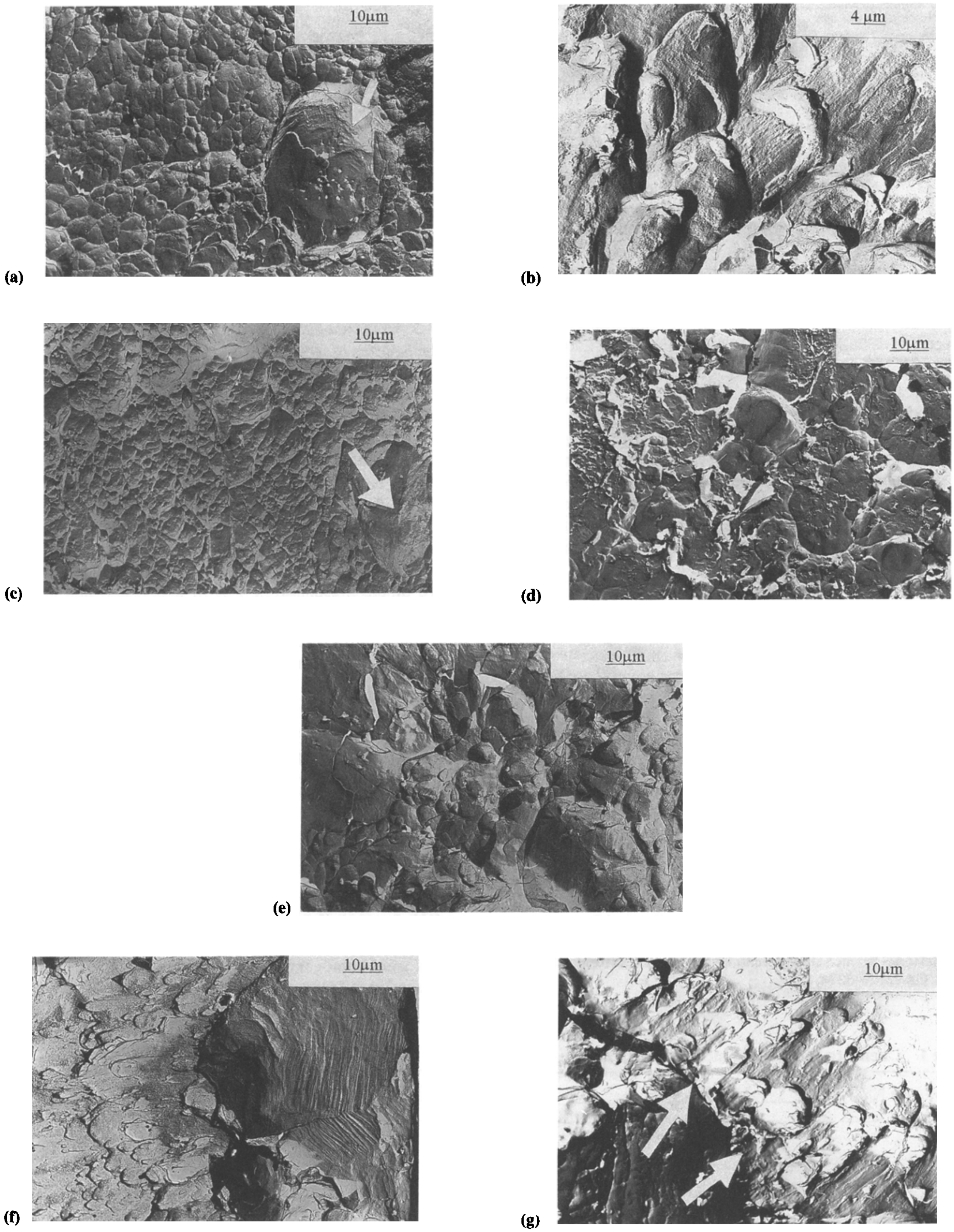

Fig. 1 Fracture surfaces of alloys 1 to 8. (a) Mostly ductile fracture in the baseline Cu-Ni-Si alloy 1; some brittle areas are observed (arrow). (b) Fully ductile transcrystalline fracture in alloy 2 (0.22% Cr addition). (c) Ductile transcrystalline behavior with minor cleavage areas in alloy 3 (0.6% Cr addition). (d) Ductile fracture in alloy 5 (0.41% Cr and 0.02% Zr additions). (e) Equiaxed dimples in alloy 8 (0.36% Cr, 0.02% Zr, and 0.01% Ti). (f) and (g) Partial ductile fracture surfaces in alloys 6 (0.05% Ti) and 7 (0.27% Ti)

2.2 *Specimen Characterization*

Mechanical testing was performed at room temperature and at 500 °C. Tensile testing at room temperature was conducted in an MTS machine with a strain rate of 5×10^{-3}/s. Elevated-temperature tensile testing was conducted with a strain rate of 5×10^{-2}/min. The samples were heated at 500 °C, held at test temperature for 15 min, and tensile tested. In addition, Brinell hardness (HB) measurements at room temperature were done with 3000 kg load applied for 15 sec.

Durability testing was performed by holding specimens for 100 h at 550 °C. After cooling at room temperature, specimens were fractured and the fracture surfaces were studied using a transmission electron microscopy replica technique on a JEM-100CX microscope.

3. Results and Discussion

Table 1 presents the yield strength, ultimate tensile strengths, and hardness values at room temperature and 500 °C of the baseline alloy (Cu-3.96wt%Ni-0.95wt%Si) and alloys with Cr, Zr, and/or Ti additions. While Cr additions contributed to a decrease of mechanical properties at room temperature, they definitely improved the strength of Cu-Ni-Si alloys (alloys 2 and 3) at high temperature. The maximum increase in high-temperature strength was observed when smaller amounts of Cr were added (alloy 2). Small additions of Zr to Cu-Ni-Si-Cr alloys restored the room-temperature ultimate tensile strength to a level close to that of the initial Cu-Ni-Si alloys (alloys 4 and 5). The yield strength of Zr-containing materials exceeded that of the baseline alloy at both room and elevated temperature. Ti additions to Cu-Ni-Si-Cr alloys were not as effective in achieving high strength values when compared to Zr at room temperature (alloys 6 and 7). However, high-temperature mechanical strength values were quite comparable to those of Zr-containing alloys. Finally, the largest mechanical strength values at both room and elevated temperature were achieved in the alloy containing all three additions (alloy 8).

Fracture surfaces of the alloys after 100 h exposure at 550 °C are shown in Fig. 1. The fracture surface of the baseline alloy displays mostly equiaxed dimples, characteristic for a ductile behavior (Fig. 1a). However, some transgranular cleavage facets indicating brittle behavior may be also observed (arrow in Fig. 1a). In addition, a low degree of deformation before fracture is apparent, indicating a lack of overall ductility for this alloy. This particular Cu-Ni-Si alloy has a slight excess of Si to the formation of only Ni_2Si compound, which may be responsible for this partial brittle behavior. As expected from lower mechanical properties, alloys with Cr additions (alloys 2 and 3) exhibit a more ductile behavior than the baseline alloy. More specifically, only ductile fracture is seen in alloy 2, with more material deformation prior to final fracture of this alloy (Fig. 1b). This behavior is consistent with earlier observations that small Cr additions improve ductility of Cu-Ni-Si alloys (Ref 3). Alloy 3 shows some brittle behavior, but this time it may be ascribed to the Cr_3Si intermetallic which generated the cleavage aspect (arrow in Fig. 1c). It is known that Cr additions above 0.5% may create this new intermetallic compound,

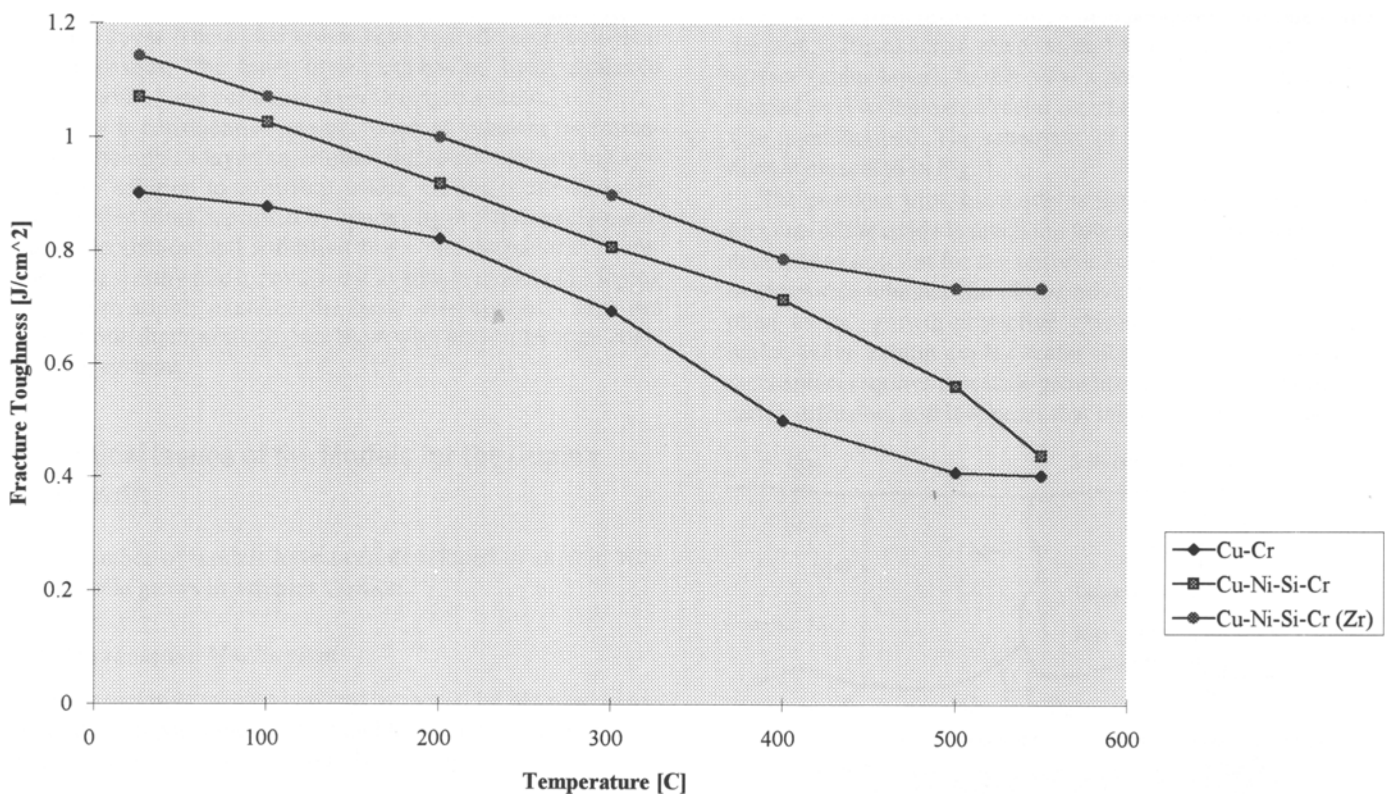

Fig. 2 Room- and elevated-temperature fracture toughness of Cu-Cr, Cu-Ni-Si-Cr, and Cu-Ni-Si-Cr (Zr) alloys in quenched/cold worked/aged condition. Source: Ref 4

which may precipitate at grain boundaries. When Cr is added to Cu-Ni-Si alloys, both Ni_2Si or Cr_3Si compounds may form. The main distinction between Ni_2Si or Cr_3Si is the time of their precipitation. More exactly, Cr_3Si precipitates directly from liquid, whereas Ni_2Si is a result of solid-state precipitation. Consequently, Cr_3Si will be stable at higher temperatures than Ni_2Si will be and, as such, will prevent grain growth during solutionizing prior to quenching.

Additions of Zr (alloys 4 and 5) and Zr + Ti (alloy 8) do not change the ductile behavior of Cu-Ni-Si alloys. Fracture surfaces indicate only equiaxed dimples typical of a ductile fracture (Fig. 1d, e). However, Ti additions move the fracture towards a more brittle behavior. Intergranular fracture is observed in specimens with Ti with parallel striations in Fig. 1(f) and intergranular precipitates shown at the arrow in Fig. 1(g). The embrittling phase may be Cr_2Ti. This phase formation, particularly at higher Ti levels, may be responsible for the lowest yield strength value at high temperature (alloy 7) among all other additions.

The general ductile behavior observed in all alloys annealed for long times at high temperature may be attributed to coarsening of the precipitates. In addition, matrix grain refinement may also be induced by additives, thus enhancing the ductile behavior. Zr and Cr are known for their grain-refining capability in Cu-base alloys. As already mentioned, if primary Cr_3Si precipitates are fine and well dispersed, they may prevent grain coarsening during solutionizing heat treatment. As seen in Fig. 2, Zr additions to Cu-Ni-Si-Cr alloys improve the fracture toughness at both room and elevated temperatures (Ref 4). However, there are differences among the alloys studied, due to different coarsening kinetics or particular precipitates formed when additives are present in basic Cu-Ni-Si alloys. In particular, Cr and Ti additions may result in some brittle behavior, probably due to Cr_3Si and Cr_2Ti phases. As already mentioned, such brittle fracture was observed in alloy 7, possibly due to Cr_2Ti compound. Phase identification in these alloys is ongoing and will be reported later.

Based on the best combination of mechanical strength values and fracture toughness, alloys containing Cr, Zr, and/or Ti additions were industrially tested in applications such as jacket coolers and dies for semicontinuous and continuous casting, and rolling of metals. The industrial tests indicated a sevenfold increase in their lifetime as compared to Cu-Ni-Si alloy for lateral blocks of copper continuous casting equipment. Welding electrodes may be another applicable use for the same type of alloys.

4. Conclusions

In conclusion, small additions of Cr, Zr, and/or Ti to Cu-Ni-Si alloys result in better refractory strength and toughness. The best high-temperature strength and fracture toughness is obtained by combining Cr, Ti, and Zr additions. Although more studies are required, these optimum properties may be ascribed to a fine grain structure combined with fine precipitates that do not cause embrittlement, such as Cr_3Si or Cr_2Ti.

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