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The effect of nickel content on the fracture behaviour of Cu–Al–Ni β-phase alloys

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The fracture behaviour of Cu–14 wt% Al alloys has been studied as a function of nickel content varying from 0 to 10 wt%. It was found that the presence of a brittle phase γ_2 at the grain boundaries is responsible for intergranular fracture in low nickel alloys. Severe intergranular embrittlement exhibited by high nickel alloys is not associated with any precipitate at the grain boundaries. In fact when high nickel alloys are cooled slowly, a ductile phase (α) forms along the grain boundaries that resists the propagation of crack through grain boundaries and the fracture is transgranular.

1. Introduction
Cu–Al–Ni β-phase alloys have received considerable attention in recent years because of their shape memory effect [1]. The shape memory effect has been observed in alloys with aluminium content close to 14 wt % and with a varying nickel content. Fig. 1, after Alexander [2], shows a relevant portion of the Cu–Al–Ni ternary phase diagram sectioned at 14 wt %. The phases which appear in the β-phase region are described in Table I. The application of these alloys is limited because of their intergranular brittleness [3]. A detailed study of their intergranular brittleness has been carried out to investigate the causes of the intergranular embrittlement in these alloys and to find remedial measures [4]. This work included a systematic study of alloys with 14 wt % Al and nickel content varying from 0 to 10 wt %. This paper reports the results of experiments carried out to find the effect of varying nickel content and the cooling rates on the fracture behaviour of these alloys.

2. Experimental procedures
The samples were melted in an induction furnace using copper (99.99%), aluminium (99.999%) and nickel (99.99+ %). The melting was carried out in an argon gas atmosphere and the metal was poured into a copper mould. After homogenization at 950° C, samples were cut to sizes of 5 mm × 5 mm × 20 mm, heated at 950° C for 45 min and either cooled within the furnace or quenched in boiling water or aqueous NaOH at − 3° C. The samples were broken by impact at room temperature and the fracture surfaces were examined using a scanning electron microscope.

TABLE I Phases present in the β-phase region

Phases	Description
α	Primary solid solution of Al and Ni in Cu, fcc structure
β	High-temperature disordered phase based on Cu_3Al, bcc structure
β_1	Low-temperature ordered phase based on Cu_3Al, DO_3 structure
γ_2	Complex cubic structure
NiAl	Ordered bcc structure
Martensite	Ordered phase with orthorhombic structure

3. Results
The fracture behaviour of these alloys as a function of nickel content was studied for various cooling rates. The results are presented in Fig. 2 where the per cent intergranular fracture is plotted as a function of nickel content for various cooling rates. Some typical fracture surfaces and the microstructures are presented in Figs 3 to 8. The fracture behaviour can be related to the microstructure as described below:

3.1. Furnace-cooled alloys
The fracture behaviour of samples cooled in the furnace is shown in Fig. 2a. Alloys with no nickel exhibit completely intergranular fracture. As nickel content increases, the fracture becomes less and less intergranular until beyond about 4 wt % Ni the fracture is completely transgranular. Metallographic examination, Fig. 4, reveals that the alloys with low nickel have a continuous layer of grain-boundary precipitates with a well-defined denuded region. As nickel content increases, the denuded region becomes less defined and a very dense network of precipitates forms in which grain-boundary precipitates are interconnected with the matrix precipitates.

3.2. Alloys quenched in aqueous NaOH
The fracture behaviour of samples quenched in aqueous NaOH is shown in Fig. 2b. Alloys with low nickel content show some tendency for intergranular fracture. There is a rapid increase in the tendency for intergranular fracture when nickel exceeds about 4%. The fracture becomes completely intergranular when nickel is more than about 8% and these samples are so brittle that they sustain intergranular cracking on quenching. Fig. 6 reveals that the alloys with nickel

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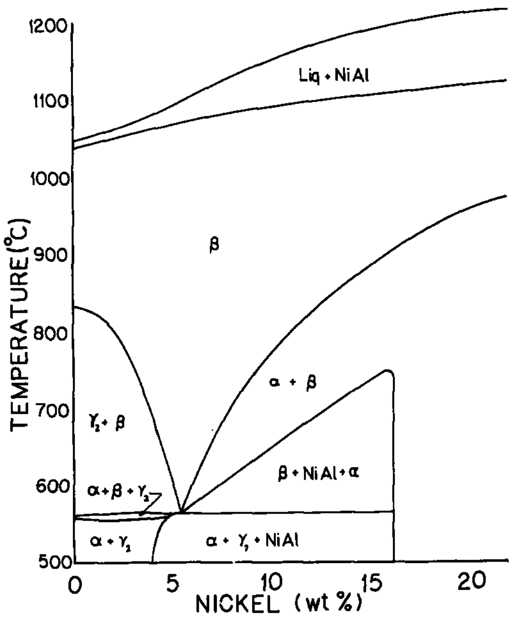
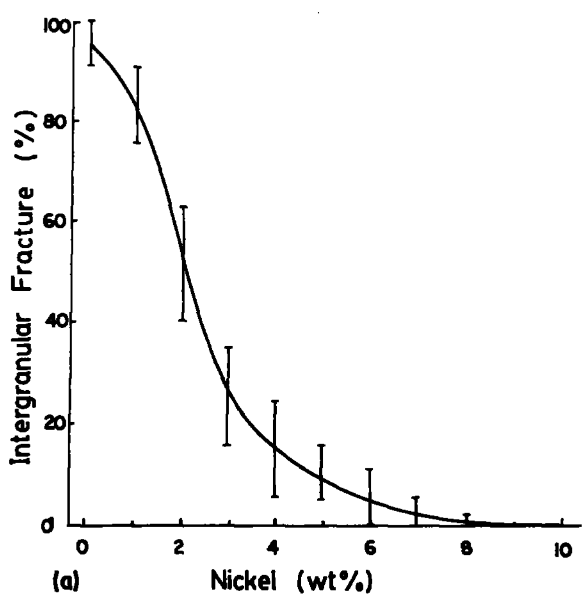
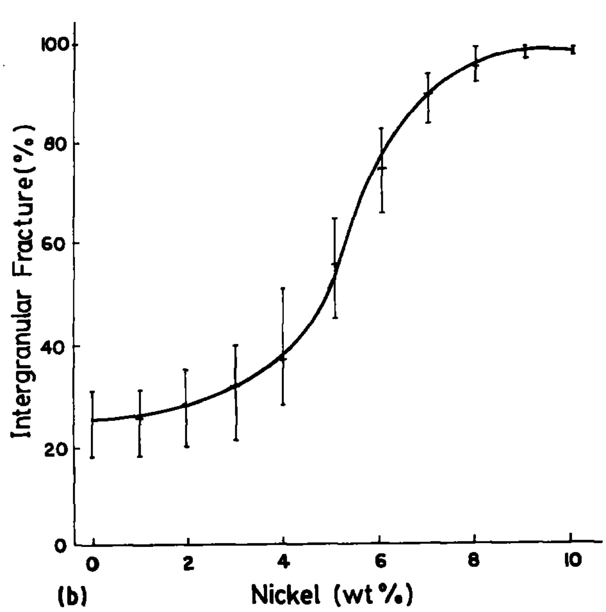


Figure 1 Cu–Al–Ni phase diagram, section taken at 14 wt % Al, after Alexander [2]. (Note: Alexander used the symbol δ instead of γ_2 used in "Metals Handbook" [5].)





< 5% have a martensitic structure while those with nickel > 5% have a single phase (β_1) structure.

3.3. Alloys quenched in boiling water

Quenching in boiling water was employed to avoid quench cracking in high nickel alloys. As shown in Fig. 2c, the fracture behaviour of these samples is, in effect, the sum of the above two results. Low nickel alloys (< 2%) show predominantly intergranular fracture. Such alloys have a well-defined denuded region and a continuous layer of grain-boundary precipitates, Fig. 7. Samples with nickel between 2% and 4% show substantially less intergranular area in the fracture surface. These alloys have a complex, dense network of precipitates. As nickel increases beyond 5%, the fracture becomes more and more intergranular until it becomes almost completely intergranular when nickel exceeds about 8%. The alloys with nickel more than 5 wt % show mostly martensitic structure on quenching in boiling water.

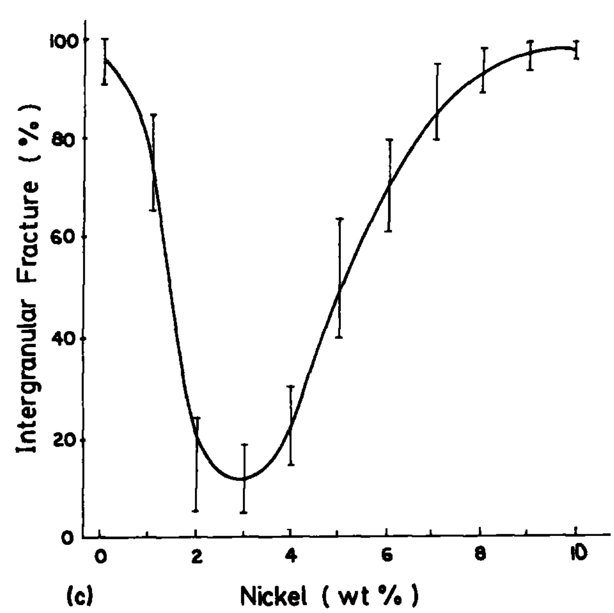
Microhardness was also determined as a function of nickel content. All these alloys were quenched from 950° C into aqueous NaOH at − 3° C which results in the formation of either martensite or β_1-phase depending on the nickel content. From Fig. 9 it may be observed that these alloys are quite hard and that there is a rapid increase in hardness in the vicinity of 4 to 6 wt % Ni.

4. Discussion

The results of the study of the fracture behaviour of Cu–14 wt % Al alloys as a function of nickel content suggest the following:

1. When the nickel content is less than 2 wt %, intergranular fracture is observed in slowly cooled alloys (boiling water quenched or furnace cooled) and this can be attributed to the precipitates of γ_2-phase observed along grain boundaries. That these precipitates are of γ_2-phase was determined using the combination of

Figure 2 Fracture behaviour of Cu–14 wt % Al alloys as a function of nickel content. (a) Samples cooled in the furnace. (b) Samples quenched in aqueous NaOH. (c) Sample quenched in boiling water.



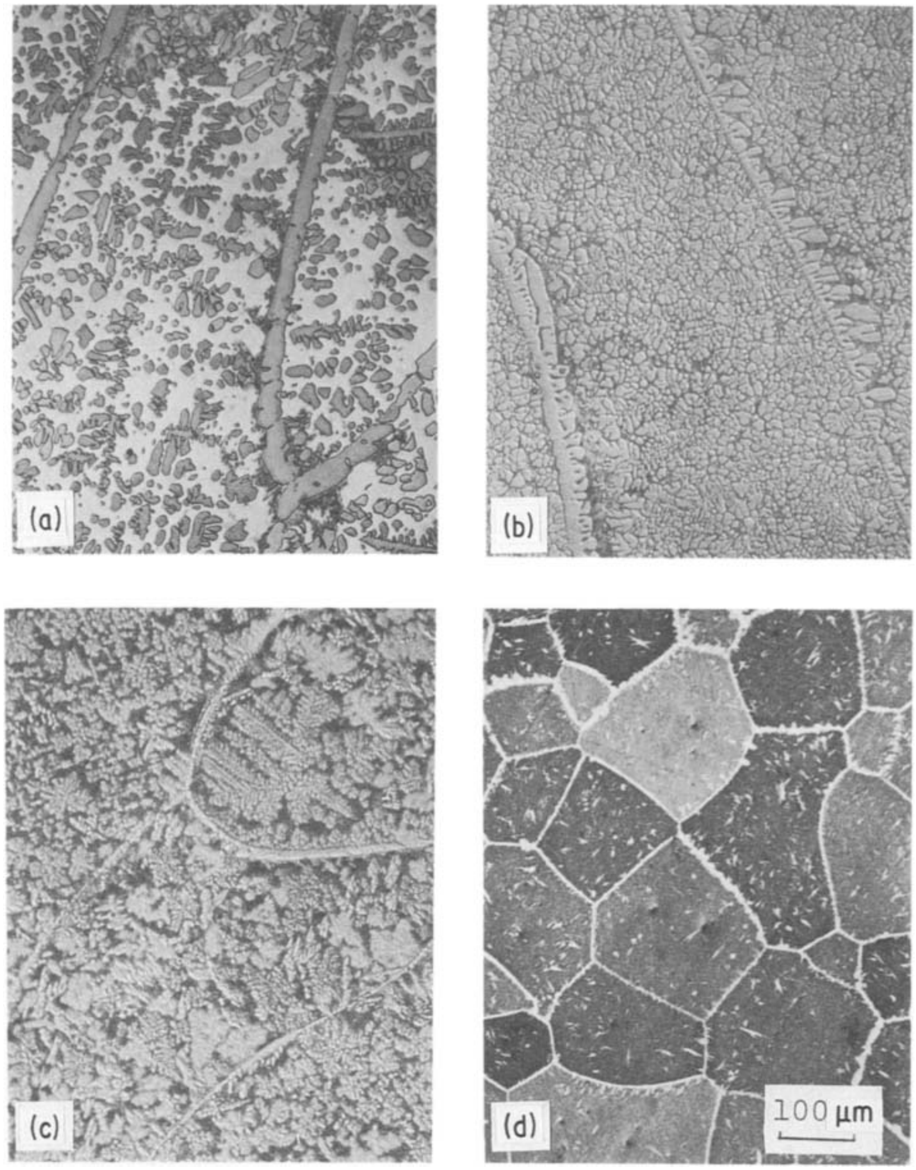


Figure 3 Microstructures of Cu–14 wt % Al alloys with various nickel contents when cooled in the furnace. (a) 0% Ni, (b) 3% Ni, (c) 5% Ni, (d) 10% Ni.

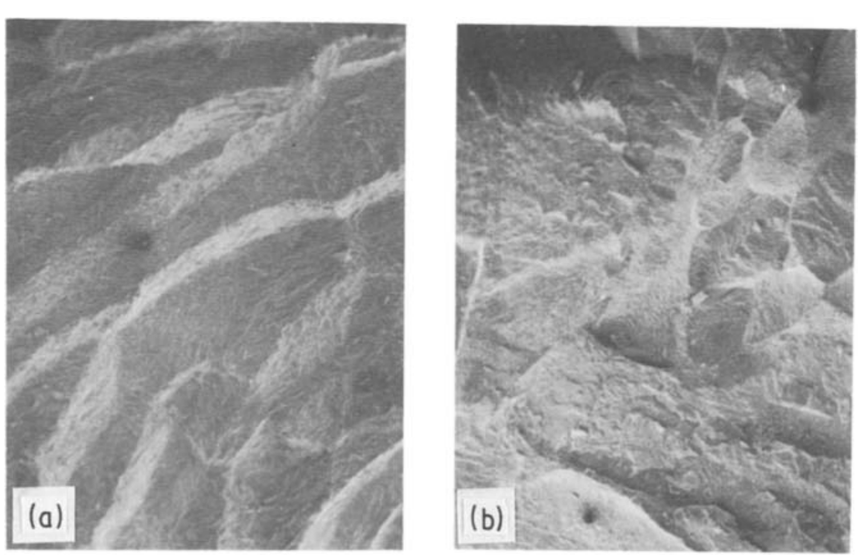


Figure 4 Fracture surfaces of Cu–14 wt % Al alloys with various nickel contents when cooled in the furnace. (a) 0% Ni, (b) 3% Ni, (c) 5% Ni, (d) 10% Ni.

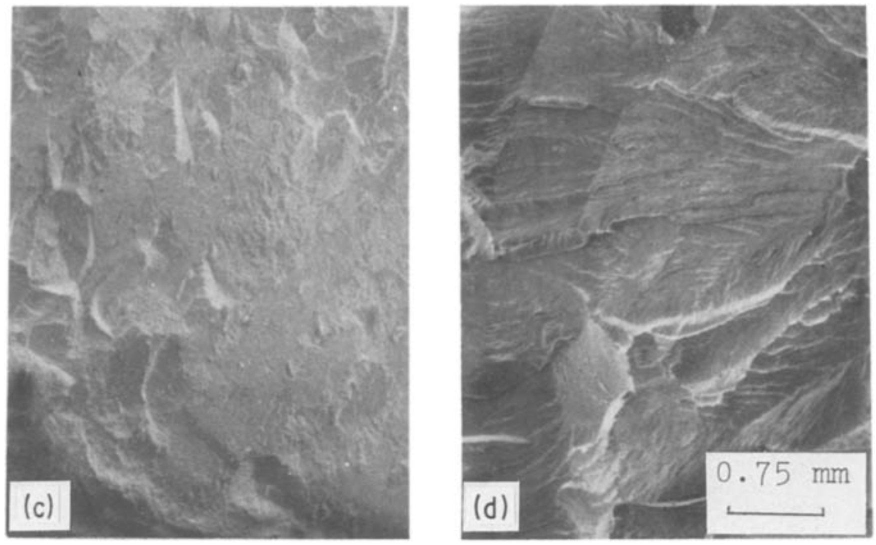


Figure 4 Continued.

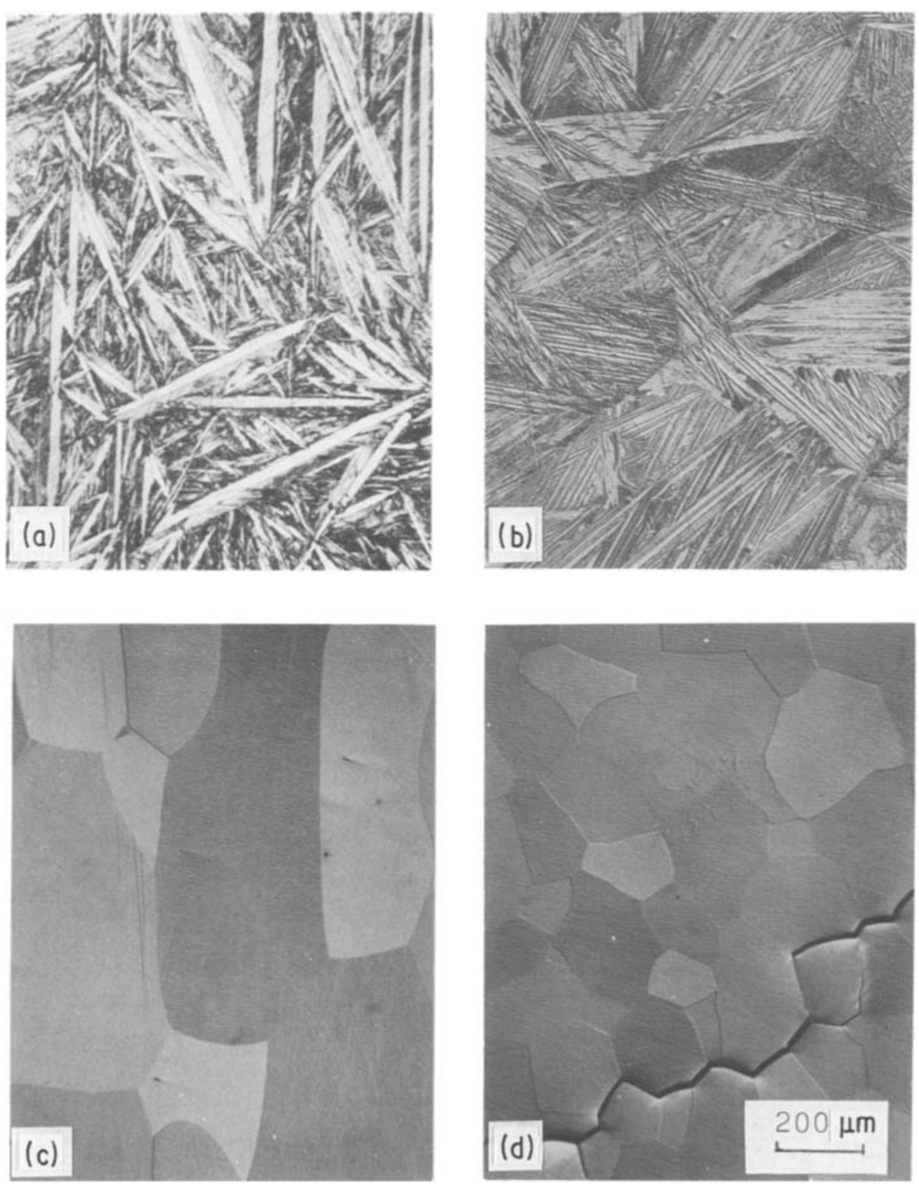


Figure 5 Microstructures of Cu–14 wt % Al alloys with various nickel contents when quenched in aqueous NaOH. (a) 0% Ni, (b) 3% Ni, (c) 5% Ni, (d) 10% Ni.

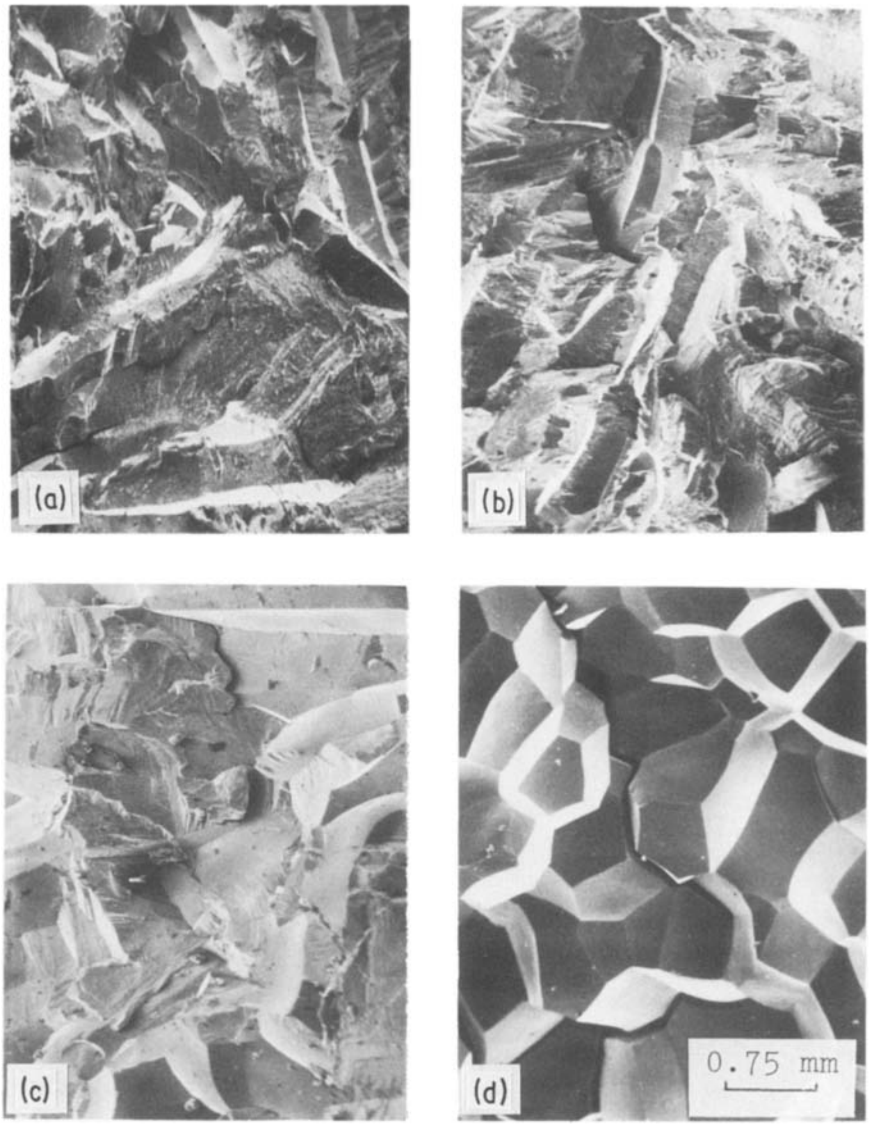


Figure 6 Fracture surfaces of Cu–14 wt % Al alloys with various nickel contents when quenched in aqueous NaOH. (a) 0% Ni, (b) 3% Ni, (c) 5% Ni, (d) 10% Ni.

electron microprobe analysis and X-ray diffraction. When such alloys are quenched in aqueous NaOH so that the γ_2 does not have enough time to precipitate out, the fracture observed is largely transgranular.

2. In alloys having $2 < Ni < 5$ wt %, slower cooling results in a very dense network of precipitates at the grain boundaries. These precipitates are interconnected to the matrix precipitates. The fracture is largely transgranular. When such alloys are quenched in aqueous NaOH, no precipitate is observed either within the grains or at the grain boundaries and the fracture is largely transgranular with susceptibility to intergranular fracture increasing with increasing nickel content.

3. Alloys more than 5 wt % Ni do not form precipitates unless cooled very slowly (furnace cooling). The fracture becomes increasingly intergranular with increasing nickel content and becomes 100% intergranular when $Ni > 8$ wt %. When such alloys are slowly cooled in a furnace, precipitates are observed along the grain boundaries as well as within the grains, and the fracture becomes completely transgranular. From the phase diagram, Fig. 1, it is seen that when $Ni > 5$ wt %, the phase which precipitates out first on cooling is α instead of γ_2. Thus the grain-boundary precipitates are expected to be of α-phase. This conclusion is supported by the microprobe analysis of a 10% Ni sample cooled in the furnace which showed that the concentration of aluminium in the grain-boundary precipitates was less than the bulk concentration.

The significance of this change in precipitate type from γ_2 to α is that the f c c α-phase is quite ductile and may be expected to offer significant plastic deformation under stress at the grain boundaries making them tougher than the matrix, whereas the presence of a brittle phase γ_2 at the grain boundaries would have just the opposite effect.

The commercial importance of these alloys lies in their shape memory properties derived from the β_1-phase. Therefore, the mechanical properties of alloys which have been quenched rapidly enough (such as quenching in cold water) to retain the β_1-phase are of primary significance. However, it was necessary to study the effect of various cooling rates in order to understand the role of intrinsic precipitates in the

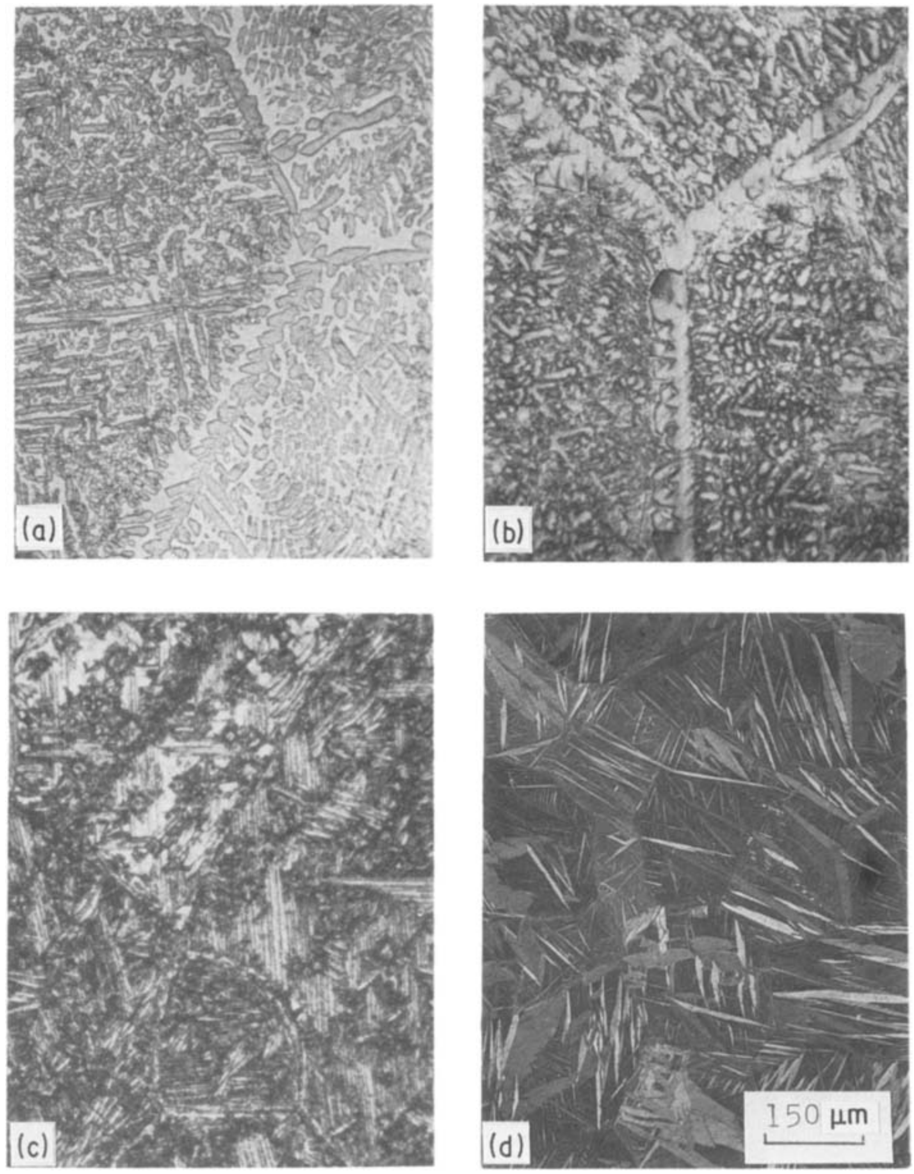


Figure 7 Microstructures of Cu–14 wt % Al alloys with various nickel contents when quenched in boiling water. (a) 0% Ni, (b) 3% Ni, (c) 5% Ni, (d) 10% Ni.

embrittlement. The present work shows that the grain-boundary embrittlement in the rapidly quenched alloys is not associated with any intrinsic precipitate at the grain boundaries. Another paper by the present authors [5] describes the results of the experiments carried out to study the role of impurities in the embrittlement in which it was found that impurities do not play any significant role in the intergranular embrittlement of these alloys.

In the absence of impurities and grain-boundary precipitates, other possible reasons for intergranular embrittlement must be investigated. The role of high elastic anisotropy has been emphasized by Miyazaki *et al.* [6]. These alloys also exhibit an unusually large grain size. As pointed out by Schulson [7], grain size has a significant effect on the intergranular embrittlement of ordered alloys. It should be noted from Fig. 9 that there is a rapid increase in the hardness of these alloys as nickel exceeds about 4 wt %. Also a rapid increase in the intergranular embrittlement is observed in Fig. 2b when nickel exceeds about 4 wt %. This may lead one to hypothesize that there is some unusual change when nickel exceeds about 4 wt %. As reported in a previous work by the present authors [8] there is good evidence of spinodal decomposition in the higher nickel alloys. Spinodal alloys, in general, are known to exhibit intergranular fracture [9], although a theoretical understanding of why this should be so is not yet available.

5. Conclusions

From this study the following conclusions can be drawn regarding the intergranular embrittlement in Cu–14 wt % Al alloys having various nickel contents: In low nickel alloys (Ni < 2 wt %) if intergranular fracture is observed, it can be attributed to the presence of γ_2-phase at the grain boundaries. In higher nickel alloys, intergranular fracture is not the result of the presence of any precipitates at the grain boundaries. Such alloys when cooled very slowly apparently form α precipitates at the grain boundaries. The presence of this ductile phase resists the propagation of cracks along grain boundaries and the fracture is transgranular.

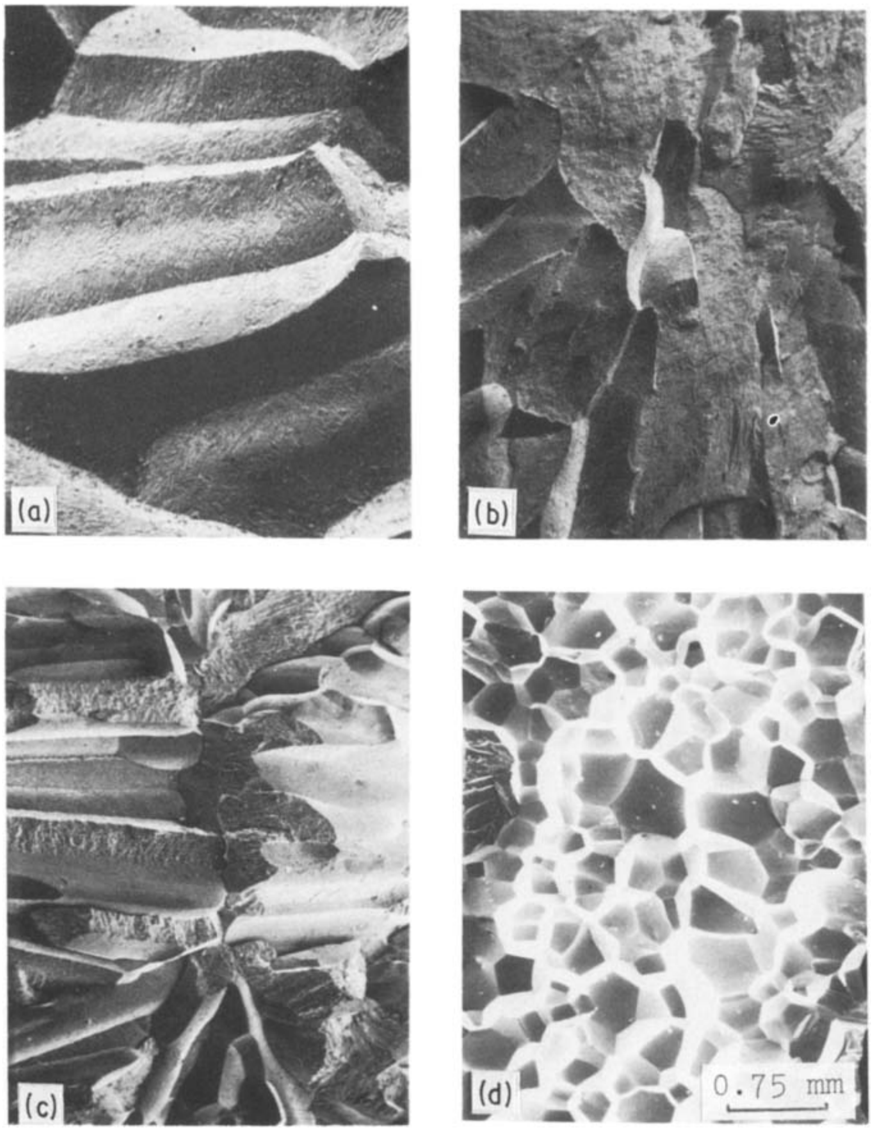


Figure 8 Fracture surfaces of Cu–14 wt % Al alloys with various nickel contents when quenched in boiling water. (a) 0% Ni, (b) 3% Ni, (c) 5% Ni, (d) 10% Ni.

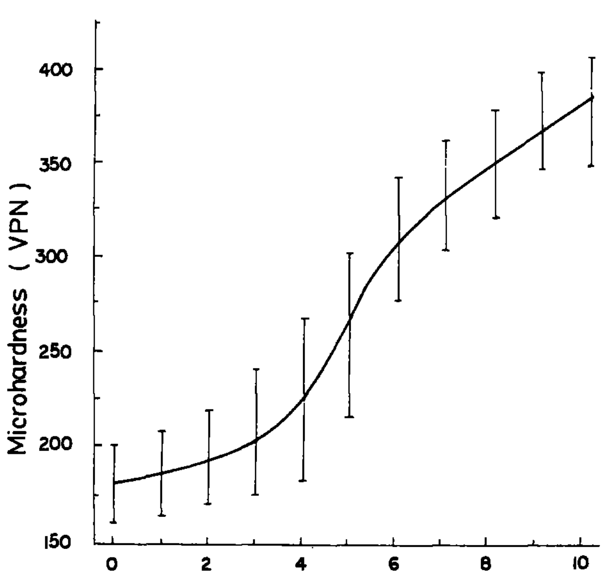


Figure 9 Microhardness of Cu–14 wt % Al alloys with various nickel contents when quenched in aqueous NaOH.

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