The intergranular embrittlement of Cu–Al–Ni β-phase alloys

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Intergranular embrittlement in the Cu–Al–Ni β-phase alloys has been investigated. Results of various experiments, which included an Auger electron spectroscopic analysis of freshly fractured grain boundary surfaces, lead to the conclusion that impurities do not play any significant role in the intergranular embrittlement of these alloys.

1. Introduction
The shape memory Cu–Al–Ni β-phase alloys are restricted in applications by their intergranular embrittlement. A detailed study has been carried out to investigate the causes of the intergranular embrittlement in these alloys and to find remedial measures [1]. Intergranular embrittlement may be caused by many factors, among which the segregation of metalloids at the grain boundaries has been found to be the most common [2]. Various impurities like bismuth, antimony, sulphur, phosphorus, oxygen and lead are known to cause intergranular weakness in copper [3]. Among these, bismuth and antimony are the most deleterious impurities. The formation of a thin layer of oxide along grain boundaries may be another reason for intergranular embrittlement in metals. This paper describes the results of experiments to study the role of impurities in Cu-14 wt % Al–10 wt % Ni since it was found that the samples of this alloy were extremely brittle, showing completely intergranular fracture.

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 required sizes, heated at 950° C for 45 min and quenched in boiling water. The samples were quenched in boiling water to avoid quench cracks which were almost always observed when samples were quenched in cold water. For Auger analysis, the samples were cut from homogenized alloys and machined into cylindrical rods 3.75 mm in diameter and 32 mm long. These round bars were heated at 950° C for 45 min and quenched in boiling water. Then a 60° notch was machined at the surface was polished using a fine (600 grit) grinding paper. The final geometry of the sample used for Auger analysis is shown in Fig. 1. These samples were broken within the evacuated chamber of an Auger spectrometer (pressure $\simeq 10^{-9}$ torr) at room temperature and the freshly fractured surfaces were

chemically analysed. The Auger spectrometer used was a Perkin-Elmer Model No. 590 at the MIT Center for Material Science and Engineering. The electron beam was operated at a potential of 5 kV and the beam current varied from 1 to 2 μA. The argon beam for sputtering was used at 5 kV with a current density of about 100 μA cm^{-2}.

3. Results
3.1. Chemical analyses
Mass spectroscopic analysis was carried out to find the bulk concentration of impurities. The analyses did not show a significant concentration of any harmful impurity. A typical analysis is shown in Table I. In particular the following concentrations of potentially dangerous impurities (in wt p.p.m.) can be noted:

S < 15, As 0.5, Sn 0.4, Sb 1.0, Pb 0.5, Bi 0.3

All the analyses showed similar concentrations of impurities. These levels of impurity concentration were expected to be too low to cause any significant concentration at the grain boundaries, but this supposition was checked by Auger electron spectroscopic analysis (AES). A typical spectrum obtained from the grain boundary surface of a sample (Fig. 2) freshly fractured in the AES chamber is shown in Fig. 3a. No detectable concentration of any impurity was observed. In particular the spectrum shown in Fig. 3a was expanded in the region of antimony signals and no peak corresponding to antimony was observed (Fig. 3b). The oxygen signal was also normal (that

TABLE I Results of mass spectroscopic analysis

Element	Concentration (wt p.p.m.)	Element	Concentration (wt p.p.m.)
B	1.0	As	0.5
Al	major	Ag	35.0
Mg	2.0	Sn	0.4
Si	50.0	Sb	1.0
S	< 15.0	Pb	0.5
Ca	3.0	Bi	0.3
Fe	5.0		
Ni	major		
Cu	major		
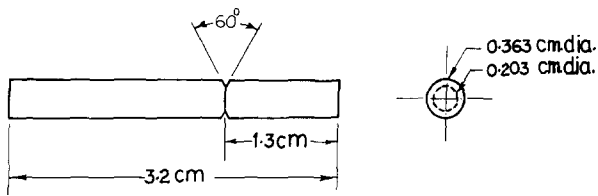
Figure 1 Geometry of sample used for Auger analysis.

Figure 2 Completely intergranular fracture exhibited by sample quenched in boiling water.

expected from the contamination of samples within the AES chamber) but in some cases an abnormally high concentration of oxygen was observed.

To confirm that the oxygen signal was not due to its segregation or due to the presence of oxide at the grain boundaries, another experiment was carried out. Ageing of quenched samples of these alloys has been found to change the fracture behaviour progressively from intergranular to transgranular [4]. A few samples were aged for 15 min at 350° C and the fracture behaviour of such a sample is shown in Fig. 4. A typical analysis of the transgranular surface is shown in Fig. 5a. It can be noted that the strength of the oxygen signal is comparable to that from the grain-boundary surface. Sputtering with argon ions also confirmed
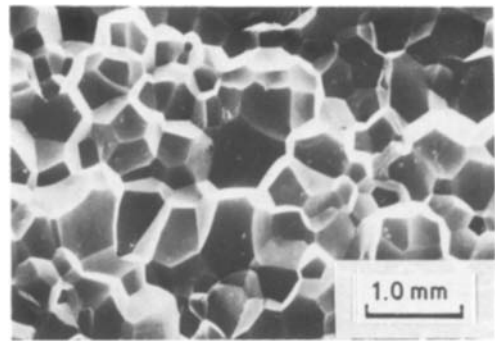
that the oxygen signal was coming from the contamination of the samples in the AES chamber. As seen in Fig. 5b, the oxygen signal decreases rapidly with sputtering time. Fig. 6a shows a typical spectrum from the grain boundary surface of the same sample (aged 15 min at 350° C). Fig. 6b shows that the oxygen signal decreases rapidly with sputtering time. When the spectrum was taken a few minutes after the surface had been sputtered for about 10 min, the oxygen peak reappeared (Fig. 6c).
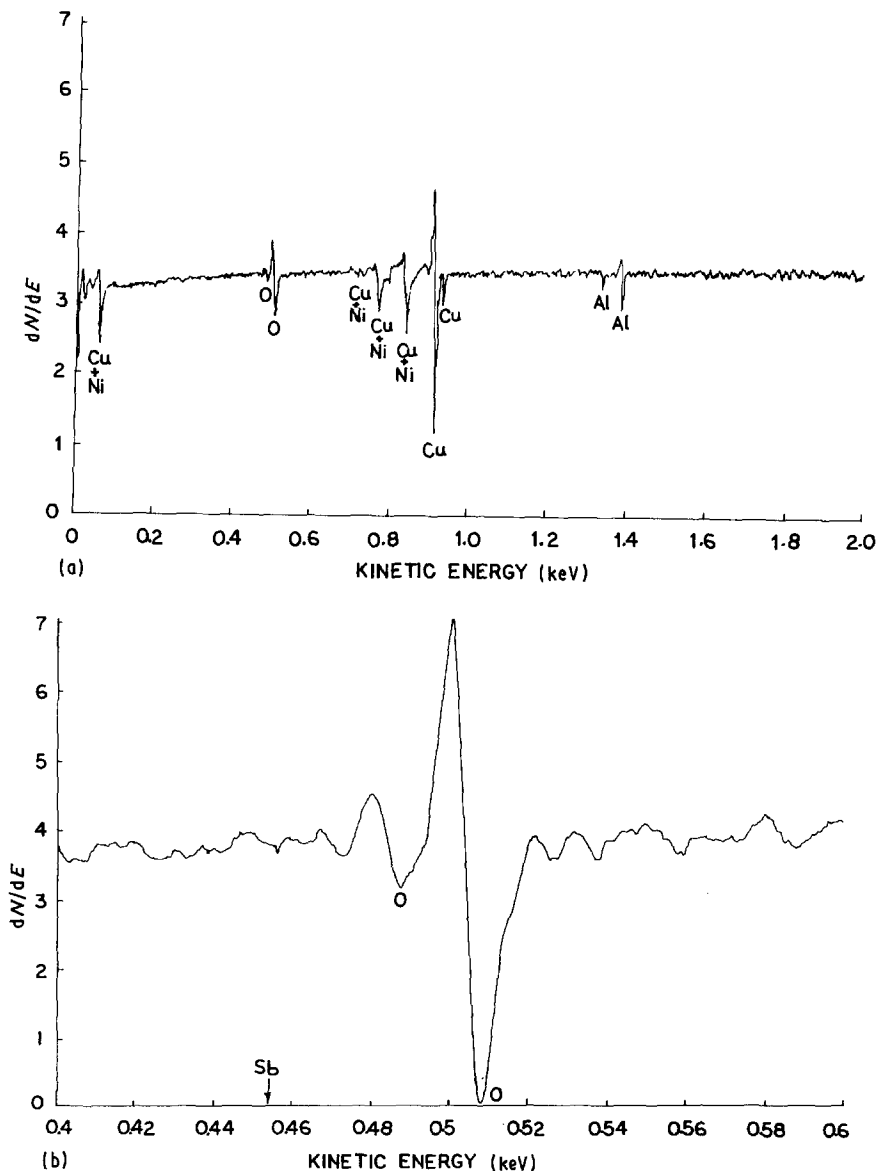

Figure 3 AES results obtained from grain boundary surface of a sample quenched in boiling water: (a) AES spectrum, (b) the spectrum expanded to show the absence of the peak corresponding to antimony.
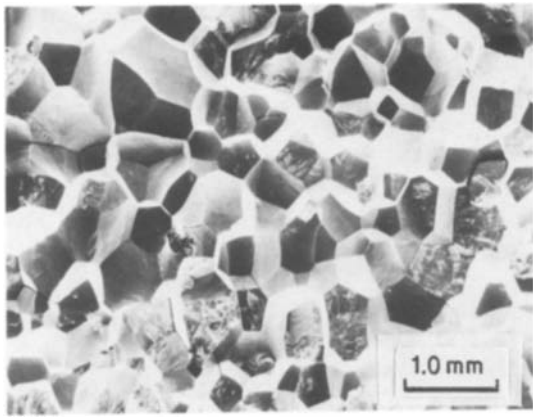
Figure 4 Partially transgranular fracture exhibited by sample quenched in boiling water and aged for 15 min at 350°C.

3.2. The role of oxygen

Care was taken to avoid oxygen in the alloys during melting. The charge, crucible and mould were thoroughly cleaned and dried before putting them in the furnace chamber. Both vacuum (pressure $\simeq 5 \times 10^{-5}$ atm.) and argon gas (99.999% purity) atmospheres were used for melting. Thus the maximum partial pressure of oxygen in the furnace chamber during melting could not exceed 10^{-5} atm. In the presence of aluminium the concentration of oxygen in the melt would be very small. Almost all the oxygen present in the melt will combine with aluminium to form solid Al_2O_3 which will float on top of the melt.

Various experiments were carried out to confirm that the diffusion of oxygen into the alloy during heat treatment could not be responsible for the intergranular fracture. Such experiments included the following:

(i) Many samples were heat-treated by encapsulating them in quartz tubes with titanium chips at a pressure of about 10^{-6} torr.

(ii) Some samples were heat-treated in flowing argon gas.

(iii) Samples of various thicknesses (2 to 15 mm) were used.

(iv) Various austenitizing temperatures and times and various quenching media were used.

None of the above-mentioned experiments showed any change in the fracture behaviour, meaning that the role of oxygen in the embrittlement of these alloys is virtually ruled out.

3.3. Effect of austenitizing time and temperature

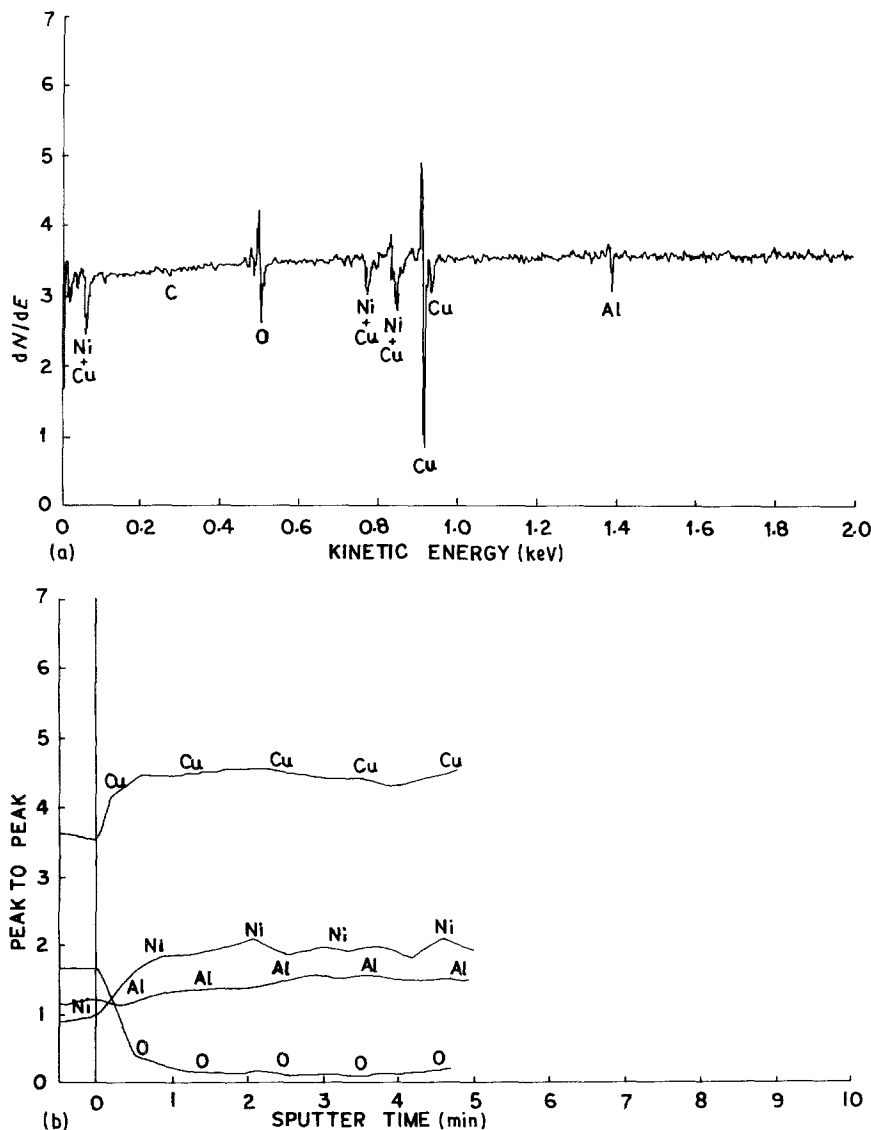A wide range of austenitizing temperatures (850 to 1020°C) and times (5 min to 37 h) and various

Figure 5 AES results obtained from a sample quenched in boiling water and aged for 15 min at 350°C: (a) AES spectrum from a transgranular fracture surface, (b) changes in AES signal strength with sputtering time.
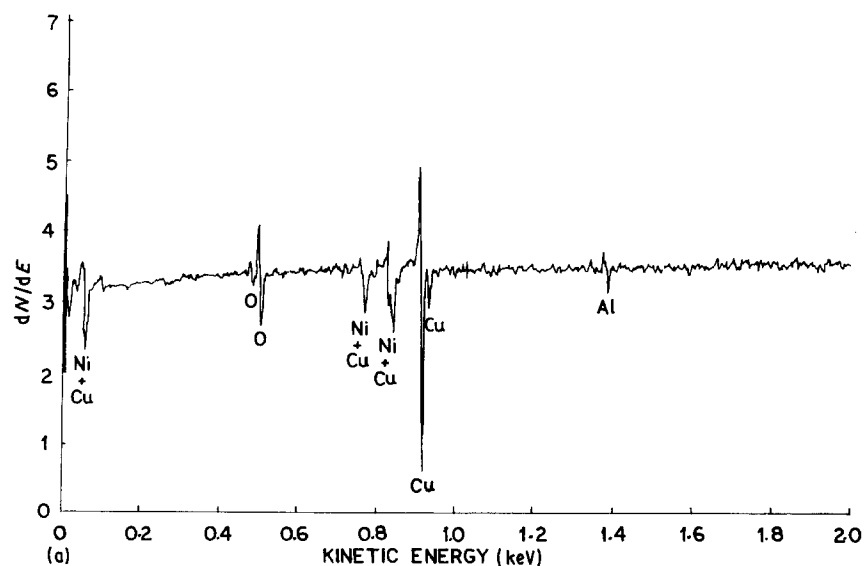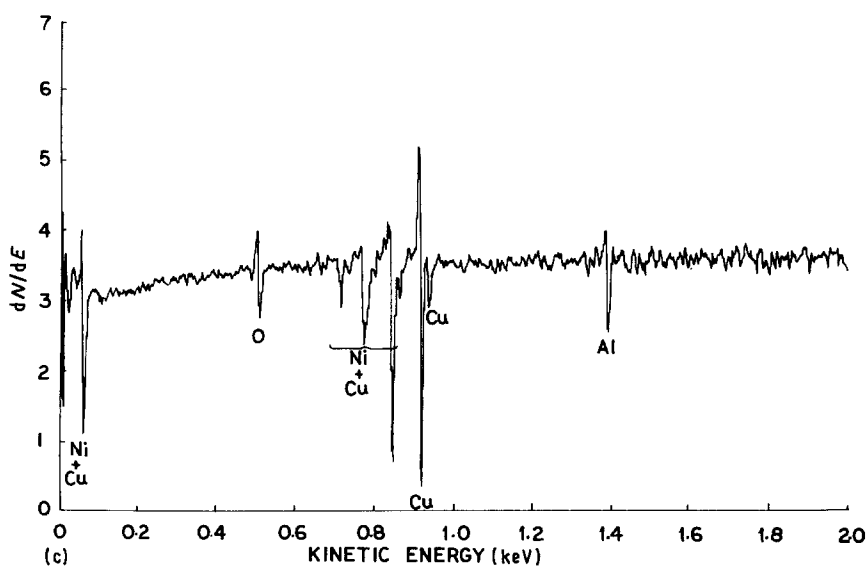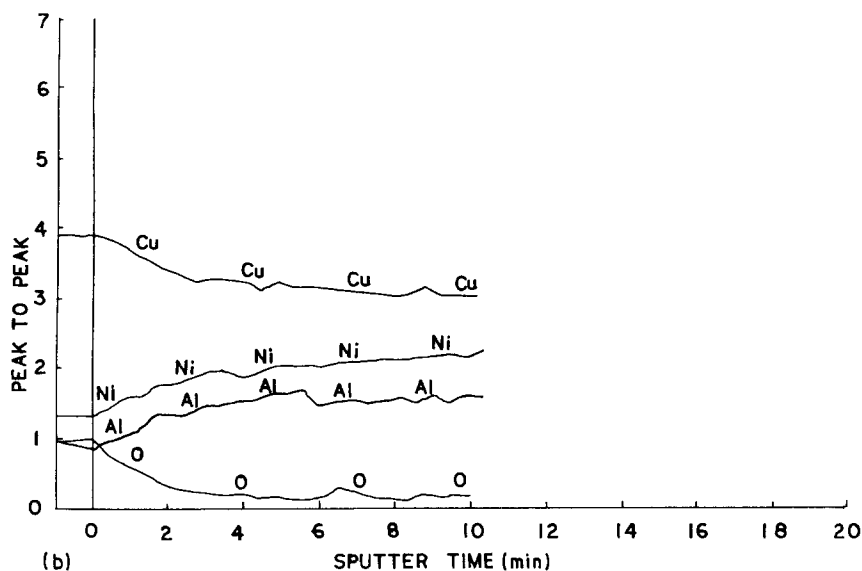
Figure 6 AES results obtained from a sample quenched in boiling water and then aged for 15 min at 350°C: (a) AES spectrum from a grain boundary surface, (b) changes in AES signal strength with sputtering time, (c) AES spectrum after sputtering for 10 min.

quenching media (aqueous NaOH at −3°C, cold water, boiling water, air cooling) were employed. In all cases, the fracture was found to be intergranular.

Sometimes grain-boundary precipitation of brittle intermetallic compounds like carbides, sulphides etc. may be a cause of intergranular embrittlement. Metallography, up to 2000 ×, did not reveal the presence of any precipitate along the grain boundaries. Also, AES analysis did not show an abnormal concentration of any impurity such as carbon or sulphur, indicating that the presence of such intermetallic compounds is very unlikely to be the cause of intergranular embrittlement in these alloys.

In addition, the characteristics of hydrogen

embrittlement are not found in these alloys. Contrary to the usual symptoms of hydrogen embrittlement, the embrittlement in these alloys is manifested even in high strain-rate tests, such as impact tests. Furthermore, there is no element in these alloys which has a strong affinity to form a hydride. The use of high strain-rate tests in a non-corrosive environment rules out the possibility of stress corrosion cracking being responsible for the intergranular embrittlement in these alloys.

4. Discussion

Results of various experiments strongly indicate that the segregation of impurities at the grain boundaries is not responsible for the intergranular embrittlement in Cu–Al–Ni β-phase alloys.

The bulk analyses showed that the concentration of the impurities which are known to be dangerous segregates in copper-base alloys was quite low. The concentration of antimony was 2 wt p.p.m. or less and that of bismuth was 0.4 wt p.p.m. or less. As an example, Joshi and Stein [5] found that copper alloys containing 3.8 wt p.p.m. Bi did not show any embrittlement, while copper containing 20 wt p.p.m. Bi showed predominantly intergranular fracture.

No detectable concentration of any impurity was observed when freshly fractured grain boundaries were analysed using AES. In particular it should be noted that the impurities known to have a very strong segregation tendency in copper alloys, such as antimony and bismuth, were not detected in these analyses.

The sensitivity factor for antimony is quite high, about 0.7 (the sensitivity factor for copper is about 0.24) [6]; thus the absence of an antimony peak in the AES spectra signifies that the concentration of antimony at the fracture surfaces was below 1%. The sensitivity factor for bismuth is low, about 0.02 [6]. This means that at least several per cent of bismuth has to be present at the grain boundaries before being detected by AES. The absence of a bismuth peak signifies that its concentration was definitely less than 5 at %. Usually about 5 at % of an impurity should be present at the grain boundaries to cause any significant change in the fracture behaviour. As reported by Joshi and Stein [5] the mechanical properties of copper were affected appreciably only when the boundary concentration of bismuth was more than about 6 at %. It is worth mentioning that a total of 32 samples were analysed by AES. In each case at least two grain boundaries were analysed.

The oxygen detected at the grain boundaries appears to be coming from its adsorption in the AES chamber. These alloys have about 28 at % Al and it is expected that oxygen will be quickly adsorbed at the fracture surfaces. This conclusion is supported by two other observations: (a) the concentration of oxygen at the transgranular fracture surfaces was found to be similar to that observed at the grain boundaries (compare Figs 5a and 6a) and (b) the concentration of oxygen decreased rapidly when the fracture surfaces were sputtered with argon ions, and reappeared when sputtering was stopped (Figs 6b and c).

The studies utilizing various austenitizing times and temperatures gave further evidence of an indirect kind that no impurity segregation process could be responsible for the grain-boundary embrittlement of these alloys. Theories of impurity segregation show that the degree of segregation (and hence the intergranular embrittlement caused by impurity segregation) decreases rapidly with increase in temperature [7]. As an example, the intergranular embrittlement of copper due to the segregation of bismuth was found to decrease very rapidly when the temperature was increased above 550° C [5]. It is probably safe to assume that it is highly unlikely to get significant impurity segregation during heat treatment close to the melting point of an alloy. In the present study some experiments were carried out in which samples were heated at about 1020° C (which is about 30° C lower than the melting point of these alloys) for 37 h. By contrast other samples were heated for 5 to 10 min at 850 to 900° C but no difference in fracture was observed (i.e. both sets showed completely intergranular fracture).

All of this evidence taken together demonstrates that impurities do not play any essential role in the intergranular embrittlement of Cu–Al–Ni β-phase alloys and so some intrinsic characteristics of these alloys must be responsible. Miyazaki et al. [8] have carried out extensive work to demonstrate that the abnormally high elastic anisotropy of these alloys leads to stress concentration at the grain boundaries of polycrystalline samples under stress. It should be mentioned that the slip systems available in these alloys are not yet established and may also be an important factor. The typically large grain sizes ($\simeq 1$ mm) are likely to contribute to stress concentration as well. In addition, the ordered phases present and the spinodal transformation can be expected to further reduce the stress relaxation capabilities of these alloys [1]. It would seem from this list that the probable cause of grain-boundary embrittlement is a combination of intrinsic characteristics rather than any single factor.

5. Conclusion

Results of the present study show that the intergranular embrittlement exhibited by Cu–Al–Ni β-phase alloys is not caused by the segregation of impurities at the grain boundaries, but must be a result of intrinsic characteristics of these alloys.

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