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Influence of Ge-Si Additions on Ageing Response and Properties in 2xxx Alloys

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2xxx Alloys containing additions of Ge-Si display a unique combination of rapid ageing response, higher peak strength, and extended thermal structure stability. Furthermore, due to a much refined precipitation, 2xxx + Ge/Si alloys show a considerable improvement in the tensile yield strength while retaining good fracture toughness, or damage tolerance. High resolution transmission electron microscopy (HRTEM) examination showed that the Ge-Si additions modify the conventional precipitation sequence in Al-Cu alloys. In Ge-Si added alloys, Ge-Si clusters quickly nucleate and grow during elevated-temperature ageing. The Ge-Si particles then act as nucleation sites for θ' precipitates, resulting in a peak-aged microstructure consisting of a dense distribution of θ' attached to fine Ge-Si particles. A similar effect was also observed in Ge-Si/Mg added alloys.

Keywords: *Al-Cu alloy; Ge-Si cluster; ageing kinetics; strength; fracture toughness.*

1. Introduction

The essential factors that control the properties of precipitation hardened structural alloys are the type, size and distribution of the strengthening precipitates in the metal matrix. The elements Si, Mg, Be, Ge, In, and Cd have been proved to modify the dominant precipitation reaction in Al-Cu based alloys [1-2]. One mechanism by which the precipitation reaction is altered is the preferential precipitation of alloy modifiers, producing heterogeneous sites for the formation of θ' phase in Al-Cu alloys [3-5].

In Al-Si-Ge alloys, much finer Ge-Si precipitates can be obtained than that in Al-Si or Al-Ge binary alloys [4-6]. The Ge-Si precipitates form a diamond cubic structure due to the compromise of the Si and Ge elements (the atomic diameter of Si is smaller than that of Al but the atomic diameter of Ge is larger). Because of the cancellation of the misfit stresses, Ge-Si precipitates do not contribute to strength remarkably, and therefore the strengths of Al-Ge-Si alloys remain relatively low. It is also reported that the ageing kinetics of Al-Ge-Si is surprisingly slow. However, the simultaneous addition of Ge and Si to Al-Cu alloys modifies the precipitation significantly [7]. Not only the ageing kinetics is accelerated but the peak ageing strength is increased as well.

The objective of this investigation is to understand the effect of alloying Ge, Si in Al-Cu based alloys, and to extend this concept to examine the effect of forming Si/Ge-Mg clusters on the precipitation behaviour and the mechanical properties in Al-Cu alloys. It will be shown that the alloys with Ge, Si and Mg additions have the similar effect on accelerating the ageing kinetics observed in Al-Cu-Ge-Si alloys. However, these alloys give a much higher strength while retaining good fracture toughness.

2. Experimental

A number of Al-Cu based alloys with additions of Ge, Si and/or Mg were cast. Alloy 1 was the reference alloy, and from alloy 2 to 5 the concentration of Si and Ge (Mg) were kept stoichiometric. Alloys 3 and 4 can be treated as removing Ge or Si in the chemistry of alloy 5. The compositions of the main elements of the investigated alloys, as analyzed in as-cast ingots, are listed in table 1. The actual compositions deviate slightly from the designed ones.

Table 1. The chemical compositions of investigated alloys (in wt.%)

Alloy	Compositions			
	Cu	Ge	Si	Mg
1	4.5	-	0.05	-
2	4.6	0.69	0.26	-
3	4.6	0.69	-	0.30
4	4.6	-	0.40	0.30
5	4.6	0.67	0.40	0.30

The cast ingots were homogenized, hot rolled and cold rolled to sheets of 2 mm in thickness. The sheet materials were solution heat treated and artificially aged. The solution heat treatment temperature was 510°C for all alloys. The ageing temperature for T6 treatment is 190°C.

Brinell macro-hardness was measured using B scale to establish ageing curves and the focus was looking at the ageing kinetics. DSC analysis and (HR)TEM were applied to characterize the ageing behaviour. Tensile test and Kahn tear test (following ASTM B871-01) were conducted to evaluate the mechanical properties.

3. Results and discussion

3.1 Alloying effect on ageing kinetics and hardening

Ge-Si or Mg containing alloys show a similar natural ageing behaviour as the reference Al-Cu alloy. However, the ageing kinetics during artificial ageing treatment is significantly changed.

Fig. 1 shows the ageing curves at 190°C for various alloys after solution treated at 510°C, water quenched, and natural aged for 2 weeks. As seen, much faster ageing kinetics is achieved in Al-Cu based alloys with Si-Ge/Mg additions. The ageing time at 190°C to reach the peak strength for Al-Cu alloy is about 12 hours, while the peak-ageing time is reduced to about 3 hours in the Al-Cu-Si-Ge/Mg alloys.

For the reference Al-Cu alloy, a hardness decreases is shown at beginning of artificial ageing. This can be attributed to partial dissolution of GP zones or clusters, which are formed during natural ageing. These GP zones or clusters are not stable (either dimensionally or chemically) upon heating during artificial ageing. Furthermore, the dissolution process leads to a long incubation time before effective hardening can occur.

However, in Ge-Si/Mg containing alloys no softening stage is observed, indicating that the dissolution process of non-stable GP zones or clusters has been largely eliminated. The alloy with the combined addition of Ge, Si and Mg exhibits the most accelerated ageing kinetics.

No substantial hardening has been achieved in the Al-Cu-Ge-Si alloy compared to that in Al-Cu reference alloy. This is due to the cancellation of the misfit stresses as reported in previous publications [4-6]. However, with extra addition of Mg or by replacing Ge/Si by Mg, a surprisingly significant increase in the peak hardness is observed.

In addition, it should be noted that the hardness decreases very slowly after peak-ageing reached in Ge-Si/Mg containing alloys. This suggested an extended favourable thermal stability of the precipitate structure in these alloys.

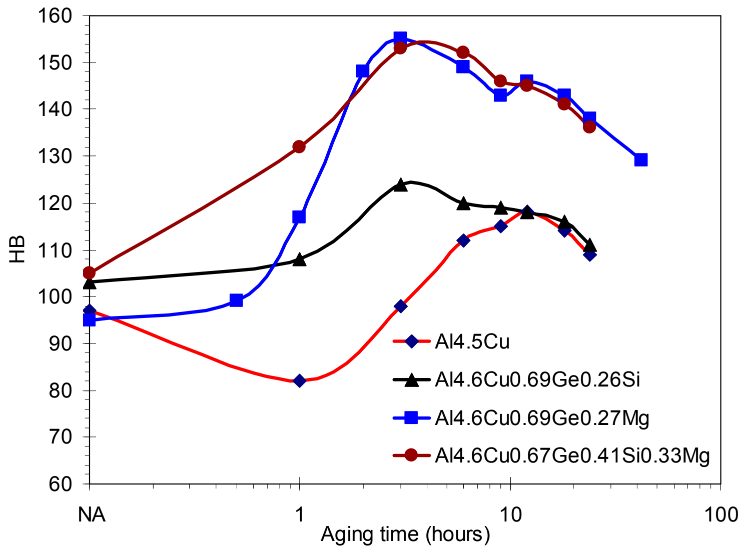

Fig. 1. The ageing curves of Al-Cu based alloys showing the effect of Ge-Si/Mg additions on the ageing kinetics.

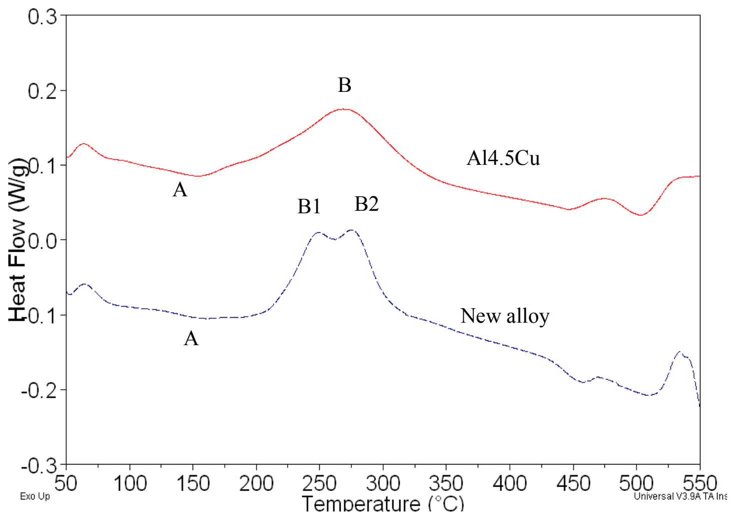

Fig. 2. DSC curves of the reference Al-Cu alloy and the new alloy with Ge-Si/Mg addition in the T4 condition.

The accelerated ageing kinetics observed in Ge-Si/Mg added alloys can be explained by the DSC profiles given in Fig. 2. First of all, the new alloys showed no clear dissolution reaction in the DSC profile, in line with the ageing curves given in Fig. 1. In the Al-Cu alloy, only one exothermic peak "B" is shown upon heating from its natural aged condition, which can be related to the formation of the hardening precipitation of θ' phase. In the new alloys, the exothermic peak "B" is split into two peaks. The peak "B1" may be related to the formation of Ge-Si/Mg clusters, whereas "B2" corresponds to the formation of θ' phase.

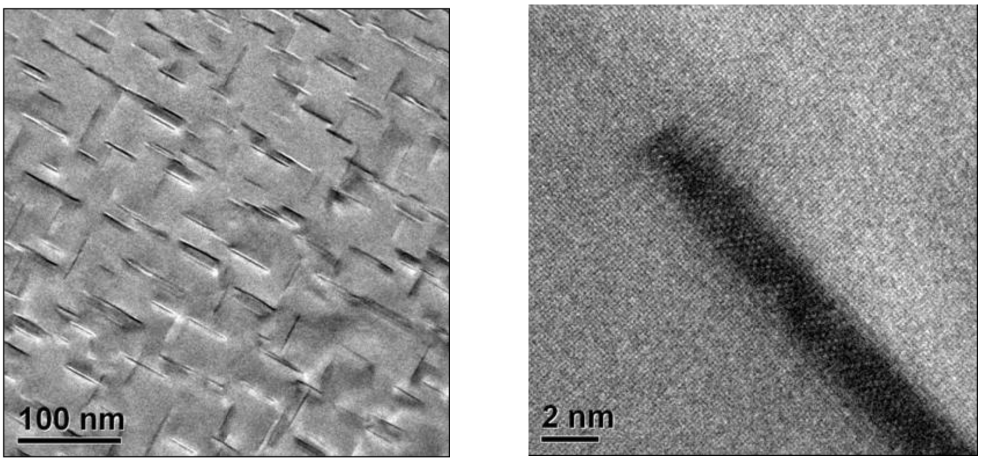

Fig. 3. Typical precipitate microstructure in the peak aged Al-Cu alloys.

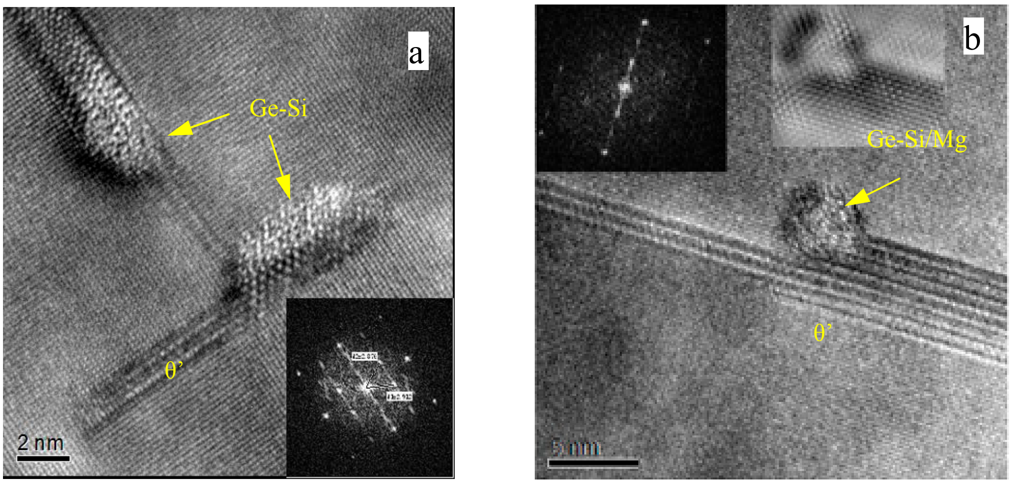

Fig. 4. The high-resolution TEM images of the microstructure in the peak aged samples. (a) Al4.5Cu0.69Ge0.26Si, (b) Al4.5Cu0.67Ge0.41Si0.33Mg.

TEM examination confirms the formation of Ge-Si clusters or Ge-Si/Mg clusters in those new alloys before the θ' precipitates are formed. Fig. 3 shows TEM images from peak-aged samples of the reference Al-Cu alloy. A typical needle-like precipitation structure is observed in this alloy.

However, as shown in Fig. 4, in the Ge-Si or Ge-Si-Mg containing alloys, Ge-Si or Ge-Si/Mg clusters were formed of the order of a few nanometers in size. These clusters serve as nucleation sites for the θ' precipitates. As a result, this accelerates the entire ageing kinetics in these alloys. Moreover, the pre-existing clusters lead to much finer θ' precipitates in these alloys than was previously observed in the Al-Cu alloy. A much refined distribution of precipitation can provide a considerable improvement in fracture toughness, or damage tolerance in high strength alloys.

3.2 Mechanical properties

Fig. 5 shows the relationships between the tensile yield strengths and the UPE values and TS/Rp of the alloys under investigation. The UPE values can be used as an indication of the resistance to fatigue crack growth rate of an alloy, while the TS/Rp values as an indication of the fracture toughness.

In general, for Al-Cu based alloys, an increase in strength leads to a corresponding decrease in the UPE values. For example, when the Cu content is increased from 4.5 wt.% to 5.7 wt.%, the yield strength is increased from about 235 MPa to about 295 MPa, while the UPE value decreased from about 250 kJ/m^2 to 150 kJ/m^2.

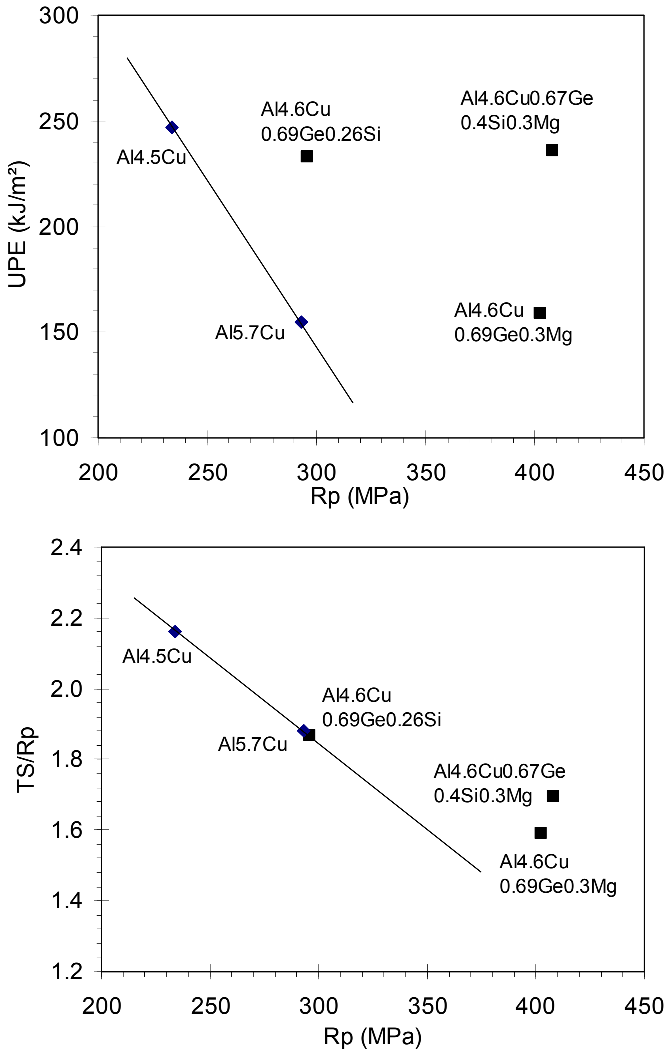

Fig. 5. Relationships between yield strength and the UPE, TS/Rp values.

For the Al-4.6Cu alloy with addition of 0.69Ge and 0.26Si, the alloy can reach about the same level of strength as Al-5.7Cu, but retain the high UPE value as that of the Al-4.5Cu reference alloy due to a much finer distribution of precipitates at the peak aged state.

Alloying with Mg to replace Ge or Si leads to a much high strength which is at the expense of lower UPE values referring to the Al4.6Cu0.69Ge0.26Si alloy. However, the combined addition of Ge, Si and Mg gave the best combination of the properties. A combination of high strength, and high UPE value is achieved in Al4.6Cu0.67Ge0.41Si0.33Mg alloy. Additions with Ge-Si/Mg in Al-Cu alloys also improve the TS/Rp values, fracture toughness. However, this effect is less significant than the effect on the UPE values.

4. Conclusions

1. A rapid ageing response and higher peak strength are achieved by adding Ge, Si/Mg to Al-Cu based alloys. The accelerated ageing kinetics is due to the pre-formation of stable Ge-Si/Mg clusters, which can act as nucleation sites for θ’ precipitates.
2. Due to a much refined distribution of precipitation, Ge-Si/Mg containing alloys show a considerable improvement in the tensile yield strength while retaining high fracture toughness, and/or damage tolerance.
3. AlCuSiGeMg alloy shows the best combination of the properties: quick ageing response, high strength, and excellent damage tolerance.

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