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Preparation of Al-20Si-4.5Cu alloy and its composite from elemental powders

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Hypereutectic Al-Si-Cu alloys with a low thermal expansion coefficient and good wear resistance are commonly prepared from pre-alloyed powders using atomization. In the present work, an attempt was made to explore the possibility of fabricating the materials from cheaper elemental powders through sintering the compacts of the mixture of a silicon powder and an Al-4.5Cu elemental powder in the liquid state. Another advantage of taking this fabrication route is that it gives an additional flexibility to incorporate Al_2O_3 particles into the alloys to form aluminium matrix composites with a further improved Young's modulus, dimensional stability and wear resistance. Due to the change in the phase constitution brought about by the silicon addition, the sintering scheme for the Al-Cu elemental powder must be modified. The results show that it is well possible to take advantage of the good sinterability of the Al-4.5Cu elemental powder, to maintain the dimensions of the Al-20Si-4.5Cu compacts and to hold their shape during liquid-phase sintering. After consolidation with hot extrusion and heat treatment, the materials show an improved Young's modulus and a lowered thermal expansion coefficient at the sacrifice of strength and ductility. The success in using the elemental powders to produce the hypereutectic Al-Si-Cu alloys and their composites opens up a new flexible and economic way to tailor the properties of the materials.

1. Introduction

The recent development in advanced materials for the automotive, electronic and recreation industries has been characterized by the increasing capacity to tailor the properties of the materials to meet the specific performance needs. It has also been recognized that the fabrication technique is an important consideration in the materials development in terms of cost and quality control [1]. In the cases like producing aluminium alloys and their composites, casting techniques are generally considered more favourable than powder metallurgy (PM) ones [2]. Only when the composition and properties of the materials needed cannot be delivered with the casting techniques, must one resort to PM, almost exclusively using atomization to produce rapidly solidified pre-alloyed powders with a refined, homogenous microstructure. A cheaper resource of ram material in the form of elemental powders has rarely been utilized.

It is well established that the use of aluminium-based elemental powders is restricted to only a few aluminium alloys that can be sintered in the form of compacts, with the formation of bonding between the initial powder particles but without much shape distortions or swelling occurring to compacts [3]. The Al-4.5Cu alloy is a typical example of such sinterable aluminium alloys. When well mixed and cold compacted, an aluminium-copper elemental powder is often sintered at a temperature above the eutectic of the Al-Cu system where a small volume fraction of liquid is formed at the interfaces between the aluminium and copper powder particles. As the sintering proceeds, the interfaces move, thereby resulting in the dissolution of the copper powder particles into the aluminium powder particles. The porosity remaining in the sintered compacts is later on eliminated by means of a mechanical working process such as extrusion. Finally, an ageing treatment enables the PM alloy to reach its peak strength, far above the common strength target of about 200 MPa at room temperature. One of the major advantages of preparing the Al-4.5Cu alloy from the elemental powder lies in a low cost relative to that prepared from a pre-alloyed powder.

Of more interest is the possibility of incorporating a ceramic powder into the pre-mixed Al-Cu elemental powder through a mixing process, to form an aluminium-matrix composite with a further enhanced Young's modulus and wear resistance. This flexibility opens up a cost-effective way of preparing aluminium matrix composites without the restrictions that the casting techniques have, for example, particle wetting and limited ceramic additions [1].

For many applications where high wear resistance and a low thermal expansion coefficient are required such as in the automotive engines and compressors, an addition of a very large amount of silicon to aluminium is desired. However, the Al-Si system is notoriously known for being unsinterable and thus no experimental work has ever been undertaken to prepare hypereutectic

Al-Si alloys and their composites from elemental powders.

In the present work, an attempt was made to explore the possibility of sintering a hypereutectic Al-Si-Cu alloy and its composite from elemental powders. The consideration was based on the fact that the Si-phase and the Al_2Cu (θ) phase are mutually insoluble in the Al-Si-Cu system. It is thus probably feasible to sinter an Al-Si-Cu alloy and its composite by taking advantage of the high sinterability of the pre-mixed Al-Cu powder, without much interference of the silicon powder to the structural integration. Obviously, the addition of silicon of a large amount alters the phase constitution and the critical temperatures of the Al-Cu system, and thus the sintering process becomes much more complicated. It was therefore necessary to determine the usable sintering parameters and the resulting mechanical properties of the sintered materials.

2. Experimental

In the present work, two types of silicon powder with different median sizes were added at a weight percentage of 19% to a pre-mixed Al-4.5Cu powder. Furthermore, an Al_2O_3 powder was added at a volume percentage of 10% to prepare composite materials. Table I gives a list of the materials investigated together with the base alloy, Al-4.5Cu (ECKA Alumix 123 AS/91S) and that added with 10 vol % Al_2O_3 (Abramax F600) for comparison.

For the materials II through V, the as-received powders were mixed with a Sartorius Turbula mixer at a motion speed of 42 rpm for 30 min. The mixtures were then compacted with a single-action, uniaxial hydraulic press at a pressure of 157 MPa into cylindrical compacts with a diameter of 49.4 mm. The compacts were dewaxed at 420 °C for 30 min and sintered at 570–590 °C (depending on the composition of the mix) for 60 min in a protective atmosphere. The sintered compacts were then extruded at 450 °C to close up the remaining pores in the compacts and convert them into bars with a diameter of 8.3 mm. The extruded bars were then heat treated at 490 °C for 30 min, followed by quenching, and finally aged at 160 °C for 12 h.

The heat-treated bars were machined into cylindrical specimens with a length of 60 mm and a diameter of 5 mm for the measurement of their Young's modulus using a Grindosonic analyzer. The materials were also subjected to tensile testing at room temperature and at a crosshead speed of 0.35 mm/min corresponding to an initial strain rate of $1.9 \times 10^{-4}\ s^{-1}$. The tensile specimens had a gauge length of 30 mm and a diameter of 6 mm. Rockwell hardness on the B scale was measured of the as-extruded and as-heat-treated materials at a load of 100 kg. The thermal expansion coefficient was determined with a Du Pont thermodilatometer. The specimens with a diameter of 5 mm and a length of 10 mm were heated up to 400 °C at a rate of 10 °C/min.

TABLE I Materials under investigation and their characteristics in the initial state

Material code	Material description
I	Al-4.5Cu-0.7Si-0.5Mg pre-mixed elemental powder (Alumix, with 1.5% wax and a median size of 95 μm)
II	Alumix + 19 wt % Si powder (MP081, with a median size of 4–5 μm)
III	Alumix + 19 wt % Si powder (MP011, with a median size of 27 μm)
IV	Alumix + 10 vol % Al_2O_3 powder (Abramax F600, with a median size of 9 μm)
V	Alumix + 19 wt % Si powder (MP081) + 10 vol % Al_2O_3 powder (Abramax F600)

3. Results and discussion

Table II gives the mean values of the green density of the compacts. The theoretical density values given in the table were calculated on the basis of alloy composition and the rule of mixture in the case of the composites (III and V). It can be seen that the addition of 19 wt % silicon to the base alloy results in a decrease in the theoretical density by 3.5%. However in practice it gives rise to a decrease in the green density by as much as 11.4 and 9.9% for the materials II and III with 4–5 and 27 μm silicon powder particles, respectively. This indicates that the addition of the silicon powder, especially the powder with a smaller median size, decreases the soundness of the compacts achievable under the given pressure of 157 MPa. The reason is that the hard silicon powder particles hinder the packing, cold welding and interlocking of the base elemental powder particles during compaction. This also explains the fact that when the base elemental powder is added with the Al_2O_3 powder, the green density is decreased while the theoretical density is increased (see the material IV in Table II). With the combined effect of the silicon and the Al_2O_3 powders, the material V has the lowest relative green density. Although the relative green densities of the materials were lowered, the compacts were sound enough to be handled with care and only the silicon powder particles at the surfaces of the compacts were easy to detach.

Sintering parameters (temperature and time) are of decisive importance for the properties and the shape retention of the sintered components. For the Al-Cu binary system, at a temperature below the eutectic temperature (548 °C), the diffusion in the solid state, needed for interparticle bonding, is very slow. Furthermore, an oxide layer on the aluminium powder particle surface tends to block the diffusion and thus the strong bonding between the elemental powder particles cannot be established within a certain sintering time. At the eutectic

TABLE II Average density values of the compacts before and after sintering (g/cm^3)

Material code	Theoretical density	Green density (relative density)	Sintered density (relative density)
I	2.780	2.398 (86.2%)	2.358 (84.8%)
II	2.682	2.125 (79.2%)	1.983 (73.9%)
III	2.682	2.160 (80.5%)	2.105 (78.5%)
IV	2.898	2.360 (81.4%)	2.335 (80.6%)
V	2.810	2.137 (76.0%)	1.973 (70.2%)

temperature, the liquid phase appears at the boundary between the aluminium and copper powder particles to lift off the oxide layer. When the temperature is a few degrees above this critical point, e.g. at 550 °C, only a very small amount of liquid exists for a short time, because the Al-4.5Cu alloy on the whole is situated in the area of the α-Al single phase. In this case, sintering cannot proceed to full. To maintain a certain proportion of liquid throughout the process, sintering must be performed in the solidus-liquidus area of the Al-Cu system, i.e., above 570 °C for the Al-4.5Cu alloy. A too high temperature will, however, lead to a very large proportion of liquid due to the gentle slope of the liquidus, tending to cause shape changes of the sintered components and the coarsening of grains and the θ-phase at grain boundaries.

On the basis of this sintering theory, the sintering parameters for the Al-4.5Cu alloy (I) and its composites (IV) were optimized at 590 °C for 1 h, where about 6 vol % liquid is maintained according to the lever rule. Table II shows that the sintered densities of the base alloy (I) and its composite (IV) are slightly lower than their green ones. This is due to the loss of the evaporated wax originally in the Al-Cu elemental powder and due to a slightly increased volume of the compacts, as a result of the dissolution of the initial copper power particles in the aluminium powder particles and the penetration of liquid along the grain boundaries.

However, when this sintering scheme was applied to the compacts containing 19 wt % silicon, a number of small spherical pieces apparently having been expelled from the compacts were found in the chamber of a sinter oven, although the original shape of the compacts did not alter. Segregation was visible with more silicon at the top of the compacts and relative more aluminium at the bottom. Atomic spectroscopy indicated varied chemical compositions of the spherical pieces, typically around 7% Cu, 8% Si and balance aluminium. Obviously, this composition is quite different from the Al(α)-Al_2Cu(θ)-Si eutectic composition (26.7% Cu, 5.2% Si and balance aluminium). It suggests that the liquid might carry the co-existing solid phases while flowing out. The lateral flow of the liquid and the segregation in the compacts (II and III) indicate a too large amount of liquid present at 590 °C. This is probably because the fluidity of the Al-4.5Cu alloy is enhanced by the silicon addition (with 5% Si added to an Al-Cu alloy, its fluidity increases by 20% [4]). Another important factor contributing to the lateral flow is that with the silicon addition the eutectic temperature is decreased from 548 to 525 °C to form the Al(α)-Al_2Cu(θ)-Si ternary eutectic instead of the Al(α)-Al_2Cu(θ) binary one [4]. This suggests that there is room to decrease the sintering temperature to a point above the Al(α)-Si area of the Al-Si-Cu system where a sufficient amount of liquid can be preserved to ensure the completion of sintering.

When the sintering temperature for the materials II, III and V was lowered to 570 °C, the lateral flow of the liquid did not occur any more and the segregation was significantly reduced. At the top of the compacts, the original silicon powder particles were no long detachable. The dimensional change of the compacts was minute, nearly the same as that of the base materials I and IV. Table II gives the average sintered densities and the relative densities of the materials, obtained under this sintering condition.

The sintered compacts were then consolidated through hot extrusion at a reduction of 40 : 1 and a ram speed of 8 mm/s. All of the materials were well densified. Due to the addition of Si, Al_2O_3 and Si-Al_2O_3 to the Al-4.5Cu base alloy, the extrusion pressure required for the consolidation and deformation was significantly increased by 17, 44 and 49%, respectively, as a result of increased deformation resistance at the extrusion temperature.

Fig. 1a, b and d show the microstructures of the consolidated materials containing a high volume fraction of the silicon crystal phase. This phase is partly formed through the ternary eutectic reaction at 525 °C:

$$\text{Liquid} - \text{Al}(\alpha) + \text{Al}_2\text{Cu}(\theta) + \text{Si}$$

This reaction produces a mixture of three solid-state phases with 5.2% silicon as a balanced constituent. The rest of the Si-phase can be formed during the cooling from the sintering temperature, but the majority of the Si-phase should be the remainder of the original silicon powder particles that have not been completely dissolved at the sintering temperature. In the microstructures, the eutectic Si-phase is located in the vicinity of the large block-like Si-phase which is likely the remainder of the original silicon powder particles, while the isolated, smaller, block-like Si-phase is likely formed during cooling from the sintering temperature.

The Young's modulus was determined from the measured period of resonance vibration R, using the following formula:

$$E = 4.106(\pi/4.734)(L^4/i^2) f^2 \rho C$$

where $f = 2 \times 10^6/R$, $i = (I/A)^{1/2}$ ($I = \pi d^4/64$, $A = \pi d^2/4$, d is the specimen diameter), L specimen length, ρ material density, and C a constant determined according to the Poisson ratio and the i/L ratio. Table III gives the average Young's modulus values of the materials. It is clear that the addition of 19% silicon increases the Young's modulus of the Al-4.5Cu alloy to the level, the same as the alloy reinforced with 10 vol % Al_2O_3 (material IV). The size of the original silicon powder particles appears to have little effect on the Young's modulus of the final material (compare the Young's modulus values of the materials II and III). The combination of the silicon and Al_2O_3 additions improves the Young's modulus significantly. The values of the present materials are in the same range as those of the Duralcan AA2014, AA2014-10%Al_2O_3, A356 and A356-10% SiC materials produced with the Duralcan process (especially developed to produce aluminium matrix composites by incorporating ceramic particles into a conventional aluminium alloy through melt agitation) [5]. The Young's modulus value of the material V is very close to that of grey cast iron (96 GPa) [2].

TABLE III The mechanical and physical properties of the materials

Material code	Young's modulus (GPa)	As-extruded hardness (HB)	As-aged hardness (HB)	Ultimate tensile strength (MPa)	Elongation at fracture (%)	CTE (μm/m°C)
I	70	45	79	492	14.2	26.6
II	76	64	83	342	1.8	22.0
III	77	61	82	337	2.2	19.1
IV	76	53	86	439	4.3	23.9
V	90	68	89	330	0.9	18.5

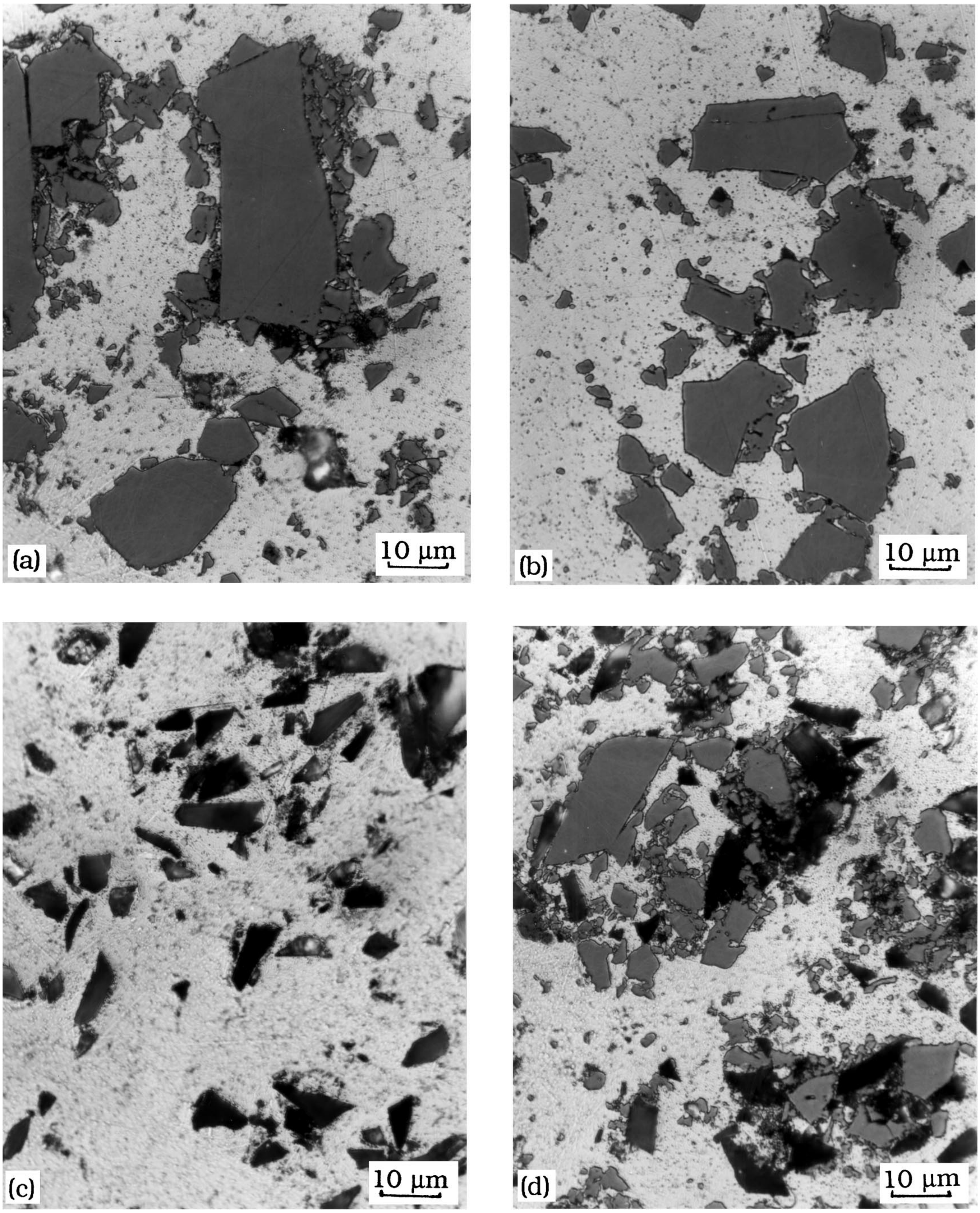

Figure 1 Microstructures of (a) material II, (b) material III, (c) material IV and (d) material V, showing the morphology and distribution of the Si-phase and/or Al_2O_3 particles in the materials after sintering from the elemental powders.

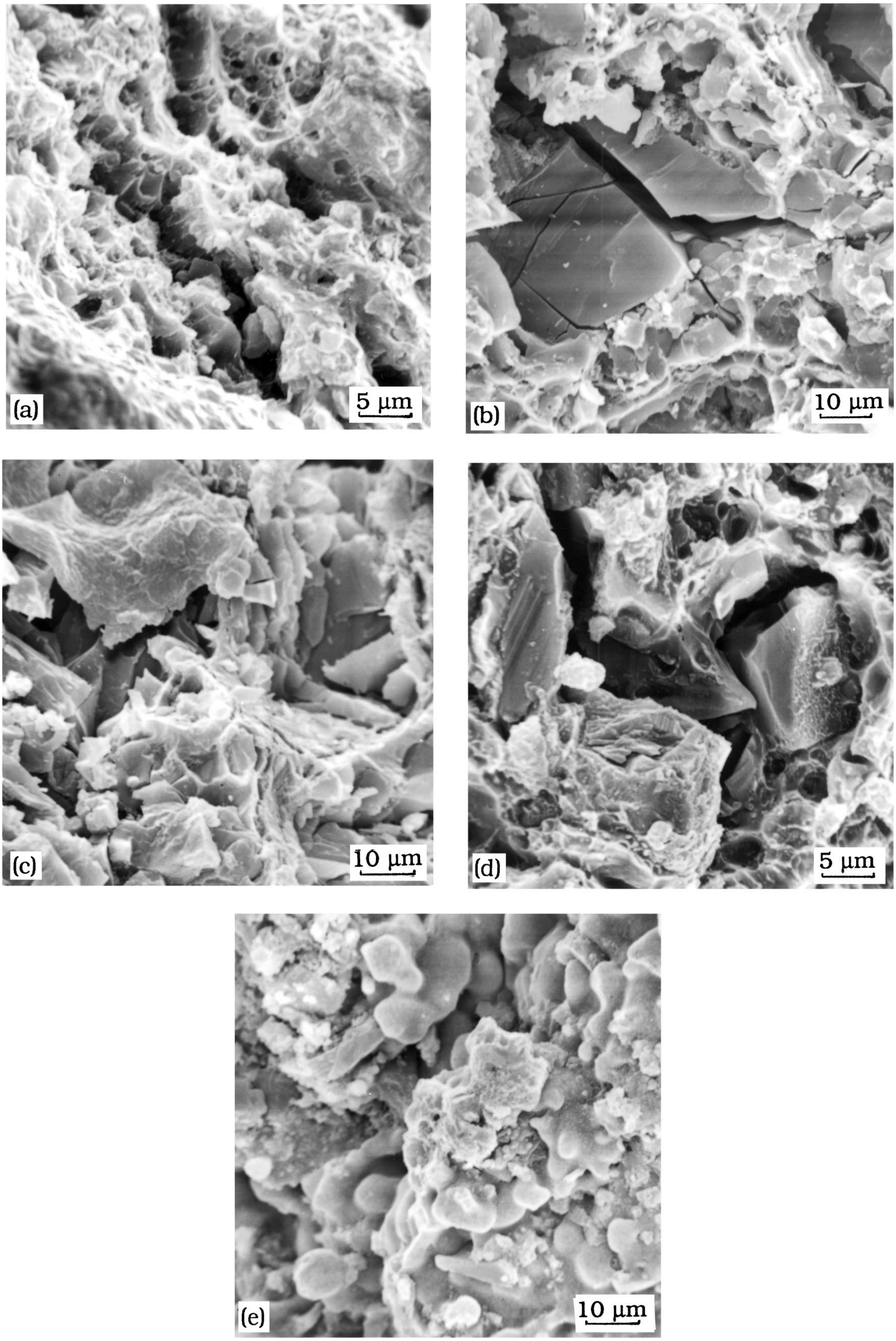

Figure 2 Fracture characteristics: (a) material I showing well developed dimples, (b) material II showing the cracking of the block-like Si-phase, (3) material III showing interfacial debonding at the Si-phase, (4) material IV showing interfacial debonding at the Al_2O_3 particles, and (5) material V showing pulling apart without any dimple formation or development.

Table III also gives the hardness values of the materials before and after the ageing treatment. For the base alloy (I) and that with the Al_2O_3 reinforcement (IV), the hardening effect given by ageing is obvious. However, for the materials with the silicon addition (II, II and V), the hardening effect of the heat treatment becomes moderate. A shift of the peak hardness with respect to ageing time may be a reason for this. Another reason is that the Si-phase gives a dispersion-hardening effect to the material in the as-extruded state as well as in the as-heat-treated state. More importantly, the presence of the Si-phase creates a dislocation hardening effect in the surrounding Al(α)-matrix due to plastic accommodation of thermally induced misfit strains. Thus, cooling from the extrusion temperature would result in the formation of dislocations around the Si-phase, contributing to the hardness of the materials in the as-extruded state. In other words, the materials have already been hardened to a certain degree before the heat treatment, and as a result the hardening effect of the precipitates in the matrix on the hardness of the material as a whole becomes less pronounced.

The tensile properties of the materials in the as-heat-treated state are presented in Table III. The strengths of the materials with the silicon addition are somewhat lower than the strength of the base alloy. This is caused by the breakage of the tensile specimens before attending their stress peak on the tensile/strain curve. A very low elongation percentage presents a typical characteristic of such type of materials with faceted particles acting as stress concentration sites during tensile deformation [2, 6]. It is the high brittleness that does not allow work hardening and plastic deformation to fully develop during tensile testing, before fracture occurs. This conclusion is supported by comparing the fractographs of the materials I and II, as shown in Fig. 2. It can be seen that the base alloy has developed dimples on the fracture surface about 45° relative to the tensile direction. These dimples appear to be associated with the precipitates within the grains induced by the ageing treatment, but the fracture is essentially intergranular with cavities at the original grain boundaries where the precipitates are also situated. For the material with the silicon addition, however, the major mechanism of fracture is the breakage of the faceted Si-phase and the decohesion at the interfaces between the Al(α) phase and the Si-phase, although there are dimples on the fracture surface perpendicular to the tensile direction.

The tensile behaviour of the material III is basically the same as that of the material II. However, when the original silicon powder particles are coarser, the final strength is slightly lower, suggesting that the undissolved Si-particles play a role in raising the local stresses during tensile deformation and thus determining the strength of the material. Fig. 2 also shows the fracture surface of the material III which is characterized by the faceted Si-phase. When the material II is further reinforced with Al_2O_3 particles, the material V becomes very brittle. There is little evidence of plastic deformation of the Al(α) phase. The fracture appears to have happened by linking the debonded interfaces between the Al(α) phase and the angular ceramic particles. Such a fracture mechanism has been determined through continuous observation of the microstructural degradation in the extruded aluminium matrix composites during tensile loading [7].

The coefficient of thermal expansion (CTE) depends on the composition and phase constitution of the material. For the materials containing a high volume fraction of the Si-phase with a diamond-cubic structure, CTE is indeed lowered, as shown in Table III. With the combination of the Si-phase and Al_2O_3 particles, CTE is brought down most significantly. For the application of the material in engines, for example, the CTE value of a material for a component should well match that of another material, usually cast iron, in order to maintain contact or clearances. The lowered CTE displays one of the most useful attributes of the materials investigated in the present work, because it reflects the dimensional stability of the materials in response to temperature changes. Table III shows that the lowered CTE together with an enhanced Young's modulus is accompanied by a loss in strength and ductility. This presents the performance trade-off at the present stage of the materials and processing development. Further work will be directed at using spherical ceramic reinforcement to delay the structural degradation in the materials during tensile loading and thus lessen the sacrifice in their strength and ductility.

4. Conclusions

1. With 19 wt % silicon powder added to the Al-4.5Cu elemental powder, the green density obtainable under the given pressure is decreased. However, the compacts are still sound enough for handling.

2. It is well possible to sinter the Al-Si-Cu elemental powders and its composites successfully. However, with the change in phase constitution at the eutectic brought about by the addition of the silicon powder to the Al-Cu powder, the liquid-phase sintering scheme should be modified in order to prevent the lateral flow of liquid and segregation from occurring.

3. Under a proper sintering condition, few dimensional or shape changes have been observed in the compacts with the silicon powder particles. No densification occurs during sintering and thus hot extrusion for consolidation is necessary.

4. The hardening introduced during the T6 heat treatment is shadowed by the dislocation and dispersion hardening of the Si-phase in the materials with the silicon addition in the as-extruded state.

5. The 19 wt % silicon addition to the base Al-4.5Cu alloy increases the Young's modulus. The highest improvement is obtained by the combination of the silicon and Al_2O_3 additions and the Young's modulus of the composite is close to that of cast iron. This gain is however accompanied by the losses in strength and ductility. A further attempt will be made to limit the losses by using spherical ceramic reinforcement.

6. The successful preparation of the hypereutectic Al-Si-Cu alloy and its composite from elemental powders offers a new possibility to tailor the properties of the materials by changing their composition relative

freely and economically through mixing, liquid-phase sintering and hot extrusion procedures.

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