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The formation of reacted film and its influence on tribological properties of extruded Al-Si-Cu-20-25Pb alloy under dry sliding

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The friction and wear characteristics of AlSiCuPb alloys, especially antiseizure, have been investigated under dry sliding for a wide range of load. It is shown that hot extrusion considerably improved antiseizure properties of stircast AlSiCuPb alloys, and a stable wear rate with the lowest level of coefficient of friction are found to be controlled by the formation of a reacted film covering almost the entire worn surfaces of specimens under high applied load. The reacted film consists of compounds containing Al, Si, Pb and O. The reacted film is generally found to play significant role in improving the ability to resist seizure for AlSiCuPb alloys containing 20 wt% and 25 wt% lead.

1. Introduction

The monotectic Al-Pb alloys have presented a great potential as advanced bearing materials since the solidified Al-Pb alloys exhibit a microstructure where the soft lead particles are fine and homogeneously dispersed in the mechanically strong aluminum matrix if gravity induced sedimentation is absent [1]. To overcome the decomposition in the liquid state on cooling through the liquid miscibility gap, unconventional techniques have been developed including stircasting, spray deposition, powder metallurgy, Marangoni-convection casting and mechanical alloying [2–6]. Among these methods stircasting exhibits evident advantage over the others due to its simple experimental equipment, low cost and mature knowledge base in processing similar to that of particles reinforced aluminum based composite containing SiC or Al_2O_3. However, most works on the characteristics of the friction and wear have been done by using stircast Al-Pb alloys as experimental materials [7–11]. The characteristics of the friction and wear, especially antiseizure property has not been well understood because of several limitations as follows:

(1) Low lead content: Some studies were made on the antiseizure and antifriction of leaded aluminum alloys with less than 10 wt% lead content. However, better bearing materials contain about 20 wt% of the soft phase, which guarantees good anti-friction properties [12].

(2) Narrow range of testing load: The applied load was not large enough to cause occurrence of seizure [9, 10, 13]. With development of engine with higher output and high efficiency, the operational conditions become increasingly severe due to high load, temperature and film pressure bringing seizure resistance of bearing alloys into current attention.

(3) A large amount of casting defects: In the ingots produced by powerful stirring considerable amount of casting defects may result during fabrication in atmosphere. The porosity may be as high as over 10% and acicular eutectic silicon particles inevitably have great negative effects on the mechanical properties of AlSiPb alloys [14–16], overshadowing their excellent friction and wear properties, especially high antiseizure property.

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The film of lubricant produced on worn surface of stircast Al-Pb alloys during sliding test has generally been considered as one of pure lead, its anti-seizure mechanism was proposed to be due to melting and flow over to the mating surface and thereby, reducing the occurrence of seizure [13]. However, the morphology and the role of the reacted film formed at high applied loads on worn surface of AlSiCuPb alloys in enhancing anti-seizure property of the alloy has been rarely reported. And more work is required to gain a better understanding of its improved anti-seizure resistance. This paper aims to examine the role of load induced solid film on the worn surface of AlSiCuPb alloys in improving the anti-seizure property for a wide range of applied load.

2. Experimental details

2.1. Materials

The AlSiCuPb alloys with lead content in the range 0–25 wt% were prepared by a stir casting technique, the details of which have been described elsewhere [17–19]. The compositions of the base alloy are given in Table I. Cylindrical ingots of 70 mm diameter with 10 wt%, 15 wt%, 20 wt% and 25 wt% lead were cast, height of 25 mm from the bottom of the ingot were cut off, and machined into a few specimens of 20 mm in diameter and 25 mm in thickness. Finally, these specimens were extruded into bars of 10 mm in diameter at an extrusion ratio of 4:1 at 400°C. The Mechanical properties, density and porosity of as-cast and as-extruded base alloy and AlSiCuPb alloys are shown in Table II.

2.2. Friction and wear testing

The friction and wear test was conducted on a pin-on disc type machine with a 70 mm diameter disc made of high carbon chromium steel heat treated to a Rockwell hardness of 57 HRC. The steel disc was kept rotating at a constant speed (78.5×10^{-2} ms^{-1}) in the investigation. The load was increased over a wide range until seizing took place as indicated by abnormal noise and vibration in the pin-disc assembly. The hot extruded bars with various lead contents were machined into pins of 6 mm diameter and 12 mm length, the flat surfaces of the machined test specimens and the steel disc were ground to a surface finish of about 0.4 μm, degreased by rinsing with acetone and dried before the commencement of each wear test. Specimens were weighed before and after the wearing test on a single pan electrical balance that gave readings to an accuracy of 0.1 mg. The average of difference in weight of the three test pins before and after the experiment determined the average weight loss for sliding over 376.8 m distance, from which the average volume of wear was calculated. The coefficient of friction is average over both the run-in and the steady state. All the wear tests were carried out under dry sliding conditions at a relative humidity of about 60% and a room temperature of 22°C.

TABLE I The chemical composition of the base alloy, wt%

Cu	Si	Mg	Mn	Sn	Al
1.0	4.0	0.5	0.4	1.0	Bal.

The worn surfaces of the wear pins after the test were examined by using JEOL8600 scanning electron microscope (SEM) attached with the energy dispersive X-ray analysis (EDX), Nikon optical microscope and VG ESCALAB MK II X-ray photoelectron spectroscopy (XPS). Rigaku X-ray diffractometer (XRD) was used to analyze the phase constituents of the test materials and the wear debris using Cu K$_\alpha$ radiation under condition of 40 kV 30 mA.

3. Results and discussion

3.1. Microstructure of hot extruded AlSiCuPb alloys

X-ray diffraction analysis as shown in Fig.1 indicates that the phase constituents of the extruded Al-4Si-1Cu-20Pb alloy consist of primary aluminum-rich phase (α-Al), lead-rich phase and silicon. After the hot extrusion the microstructure has changed considerably as illustrated in Fig. 2. The structure of extruded AlSiCuPb alloys as shown in Fig. 2b reveals lower amount of casting defects like porosity, reduced grain size of α-Al and breakdown of acicular eutectic silicon into smaller particles distributed on the grain boundary of α-Al. The size of lead particles has also decreased, even sometimes to a size similar to that of the silicon particles as can be seen from the silicon and lead mapping of the hot extruded Al-Pb alloy given in Fig. 3. However, the average size of lead particles increased from 6 μm to 8.5 μm in the case of hot extruded AlSiCuPb when

TABLE II Mechanical properties, density and porosity of as cast and as extruded base alloy and Al-Si-Pb alloys

Alloy composition	Hardness (HB)	Ultimate tensile strength (MNm^{-2})	Elongation to fracture (%)	Density (g cm^{-3})	Porosity (%)
As-cast Al-4Si-1Cu	45	160	4.3	2.61	4.25
As-cast Al-4Si-1Cu-10Pb	42	124	2.7	2.58	12.53
As-cast Al-4Si-1Cu-15Pb	47	105	2.1	2.47	19.74
As-cast Al-4Si-1Cu-20Pb	37	82	1.3	2.57	20.09
As-cast Al-4Si-1Cu-25Pb	34	79	0.5	2.51	25.2
As-extruded Al-4Si-1Cu	67	185	21.4	2.67	2.14
As-extruded Al-4Si-1Cu-10Pb	65	174	18.1	2.62	4.36
As-extruded Al-4Si-1Cu-15Pb	59	169	15.0	2.91	5.42
As-extruded Al-4Si-1Cu-20Pb	54	162	14.2	3.08	4.06
As-extruded Al-4Si-1Cu-25Pb	40	156	12.3	3.11	7.68

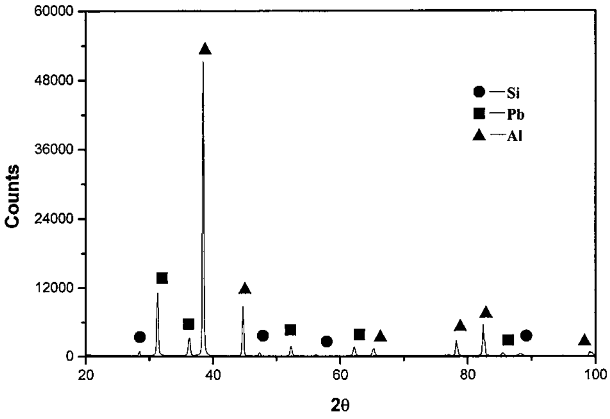

Figure 1 X-ray diffraction pattern for as extruded Al-4Si-1Cu-20Pb alloy.

the content of lead increased from 15 wt% to 25 wt%, while the average size of lead particles increased from 50 μm to 80 μm in the case of stir cast AlSiCuPb. Because of the difference in the microstructures of stircast and extruded alloys, mechanical properties have correspondingly been improved after extrusion as shown in Table II. This can be attributed to the combination of many factors interacting on each other. In the process of fabrication, due to violent stirring of Al-Pb melt at a high rotating speed, high porosity content usually in the range from 10% to 25% have been observed, and the properties of as cast Al-Pb were rapidly deteriorated. However, hot extrusion reduced the porosity to 4%–7%, and combined some other advantages such as decrease in the grain size of both α-Al grains and lead particles, and the breakdown of needle-shaped eutectic silicon into small size. All these factors contribute to the improvement of the mechanical properties remarkably.

3.2. Friction and wear behavior

To understand the seizure behavior of AlSiCuPb alloys, it is necessary to pay attention to the characteristics of friction and wear prior to the occurrence of seizure. The variations in coefficient of friction and wear rate

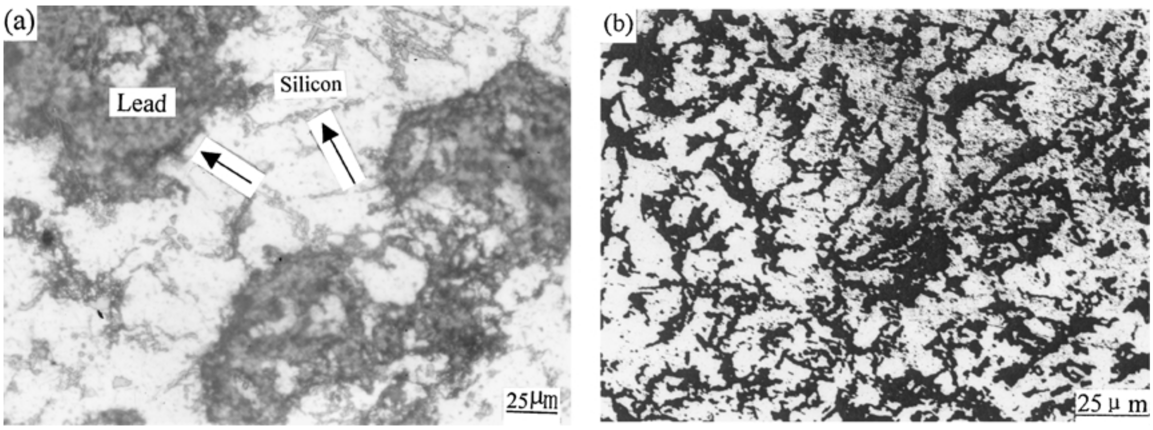

Figure 2 Microstructures of Al-4Si-1Cu-20Pb alloys (Optical Microscopy) in (a) as cast condition and (b) extruded condition.

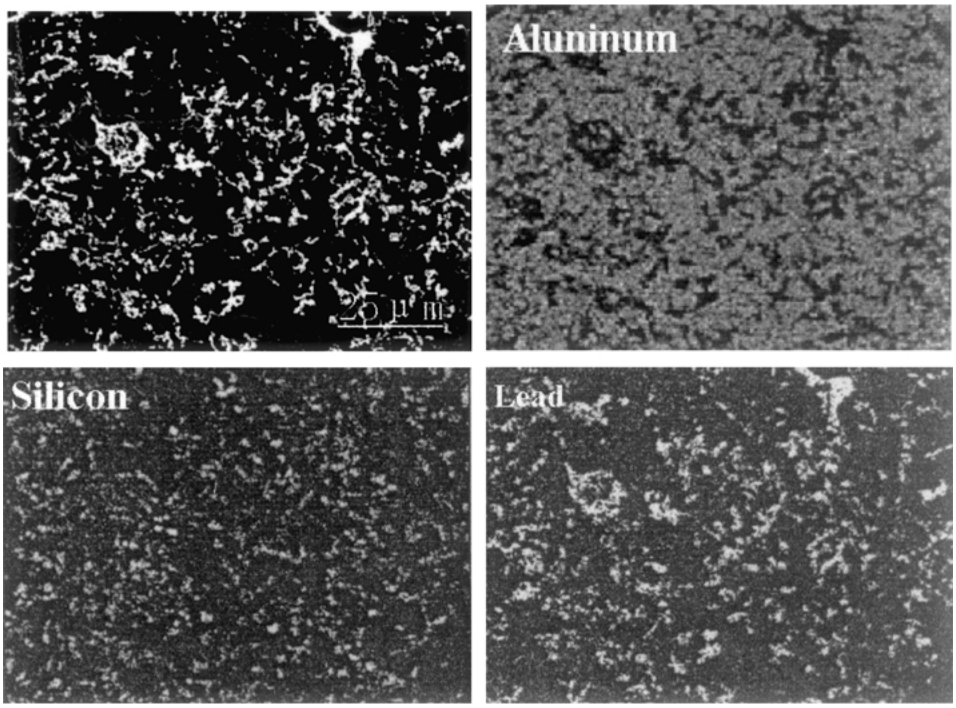

Figure 3 SEM microphotograph and the corresponding Al, Pb, and Si dot-map images showing microstructure of extruded Al-4Si-1Cu-20Pb alloy.

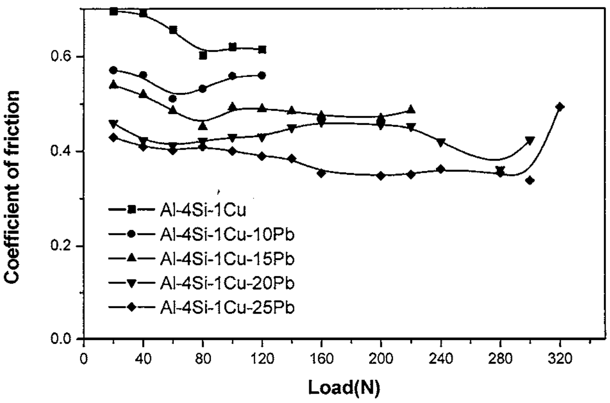

Figure 4 The variation in coefficient of friction with load for extruded Al-Si-Pb alloys.

with load for hot extruded alloys are shown in Figs 4 and 5, respectively. It is noted that the friction coefficient decreases considerably with increasing lead content, and the lowest levels in friction curve clearly occurred before seizure in a load range of 220 N to 280 N and 160 to 300 N for AlSiCuPb alloys containing 20 wt% and 25 wt% lead, respectively. The wear rate of base alloy as well as AlSiCuPb alloys containing 10 wt% and 15 wt% lead increases monotonically with load until seizure takes place. However, for the AlSiPb alloys containing 20 wt% and 25 wt% lead, the wear rate increases with increasing load, and reaches a plateau at higher load before the occurrence of seizure. This plateau region contributes a great deal to the anti-seizure property. For there is no plateau in wear rate curves of as cast AlSiCuPb alloys as shown in Fig. 5b, and their seizure loads are less than those of hot extruded counterpart. The seizure load observed for Al-4Si-1Cu-20Pb alloy processed by the stircasting and extrusion processing routes is listed in Table III. It may be noted is that the load ranges observed for the lowest levels in friction perfectly corresponds with those of the plateau region in wear rate curves. This observation suggests that different wear mechanisms work for AlSiCuPb alloys containing higher lead content and for the base alloy. The characteristic plateau in wear rate curve is often related to formation of certain kinds of surface films and similar observation has been made for the wear rate curves of aluminum based particle-reinforced composites [20–22]. The SiC or Al_2O_3 particles in composites helps to form a mechanical mixed layer (MML) on the worn surface during sliding process, and the wear rate increases very slowly with the applied load displaying a plateau. Mechanical mixed layer (MML) plays an important role in the wear of SiC particle-reinforced aluminum composites. Venkataraman *et al.* have performed hardness measurement of MML [22] and have shown that the MML formed on the worn surface of SiC-reinforced aluminum composite is substantially harder than the bulk material because it contained a fine mixture of Fe, Al and SiC phases. The absence of MML during sliding wear of the base alloy has been considered as the reason that the wear resistance of base aluminum alloy is worse than that of the composite [20, 22]. In this investigation it was found that the plateau in wear rate curve and the lowest level in friction curve have close relation with the formation and the extent of coverage provided by a black reacted film on the worn surface.

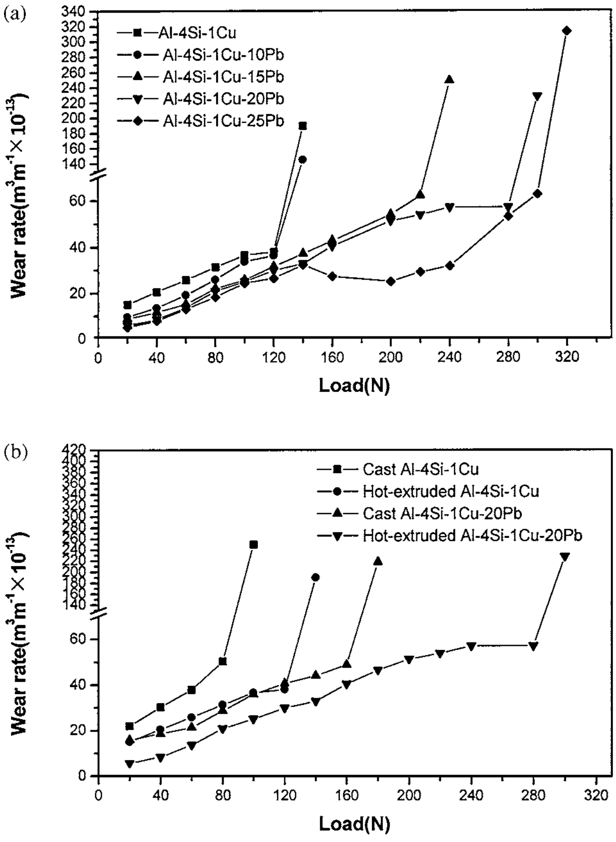

Figure 5 The variation in wear rate with load for (a) extruded Al-Si-Pb alloys and (b) as cast and extruded base alloy and the Al-4Si-1Cu-20Pb alloy.

TABLE III Seizure loads for as-cast and extruded Al-4Si-1Cu-20Pb alloys

Alloy	Seizure load (N)
As cast Al-4Si-1Cu-20Pb alloy	180
As extruded Al-4Si-1Cu-20Pb alloy	300

3.3. Morphology and structure of reacted film on worn surfaces

Macroscopic observation revealed that the appearance of the worn surface varies with load; especially at higher load level, a black film is clearly observed on the worn surface for specimens containing 20 wt% and 25 wt% lead. It plays a significant role in decreasing coefficient of friction, improving wear resistance and anti seizure property. In the case of Al-4Si-1Cu-20Pb alloy, when the load was below 60 N, black powder like substance adheres to worn surface. But beyond 60 N, the amount of powder on the surface decreases with load, and the worn surface becomes rough. At the load of 80 N, the powder disappeared and a black film could be seen in some areas locally on the worn surface. With increasing load, the area covered by black film increased gradually. But the worn surface seemed still rough until the applied load reached 200 N. When the load increased to beyond 200 N, the worn surface becomes smoother and the black film covered almost the entire worn surface. The formation of black film corresponds well to the observed plateau region in the wear rate curve and the lowest level of friction coefficient, and similar observation could be made for Al-4Si-1Cu-25Pb alloy. Microstructure further proved the existence of the black film of lubricant, and revealed that at low load, the film of lubricant looked light and thin, covering the alloy surface only partially. But at higher load, the film looked dark and thick, covering almost the entire surface. The black and thick film is often cracked at an angle of 45 degree to the sliding direction, indicating low ductility, not expected from lead film. The variation in coverage of black film of lubricant with load is illustrated in Fig. 6.

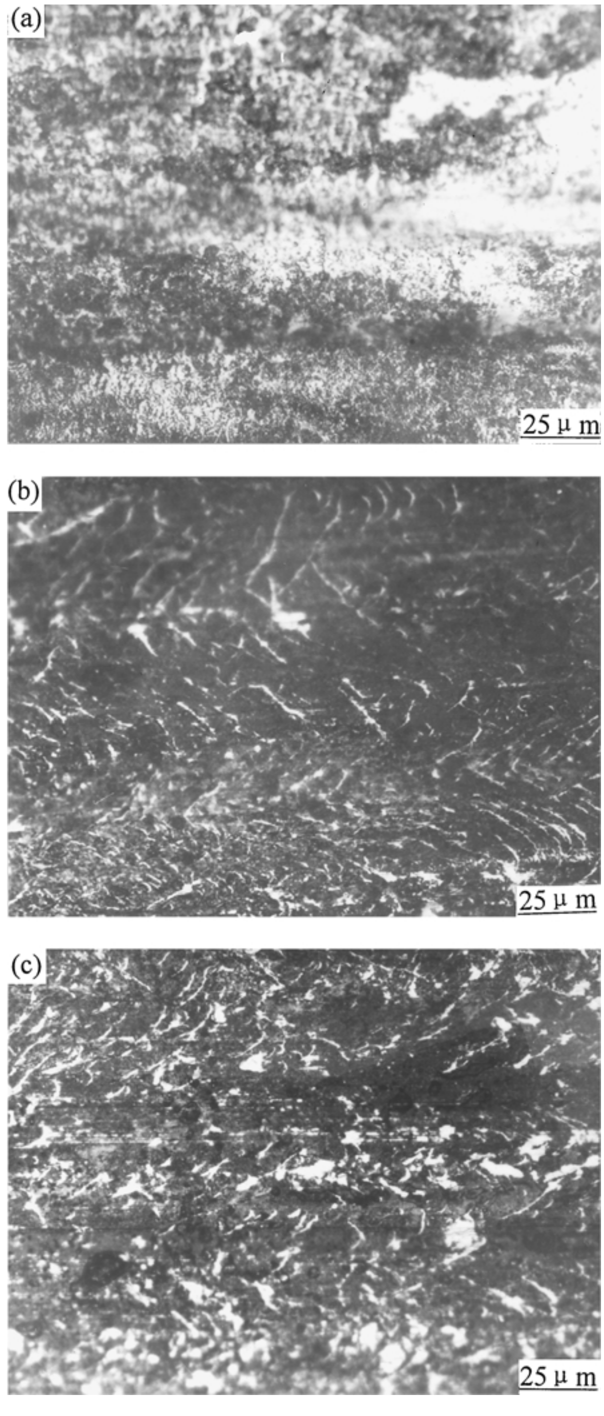

Figure 6 Morphology of black lubricating films on worn surfaces of Al-4Si-1Cu-20Pb at different loads of (a) 120 N, (b) 200 N, and (c) 240 N. (Optical microscopy).

To determine the chemical nature of the black film of lubricant, XPS analysis of the worn surface of Al-4Si-1Cu-20Pb specimen was conducted. According to Fig. 7 the film consists of Al_2O_3, a little Fe_2O_3 and

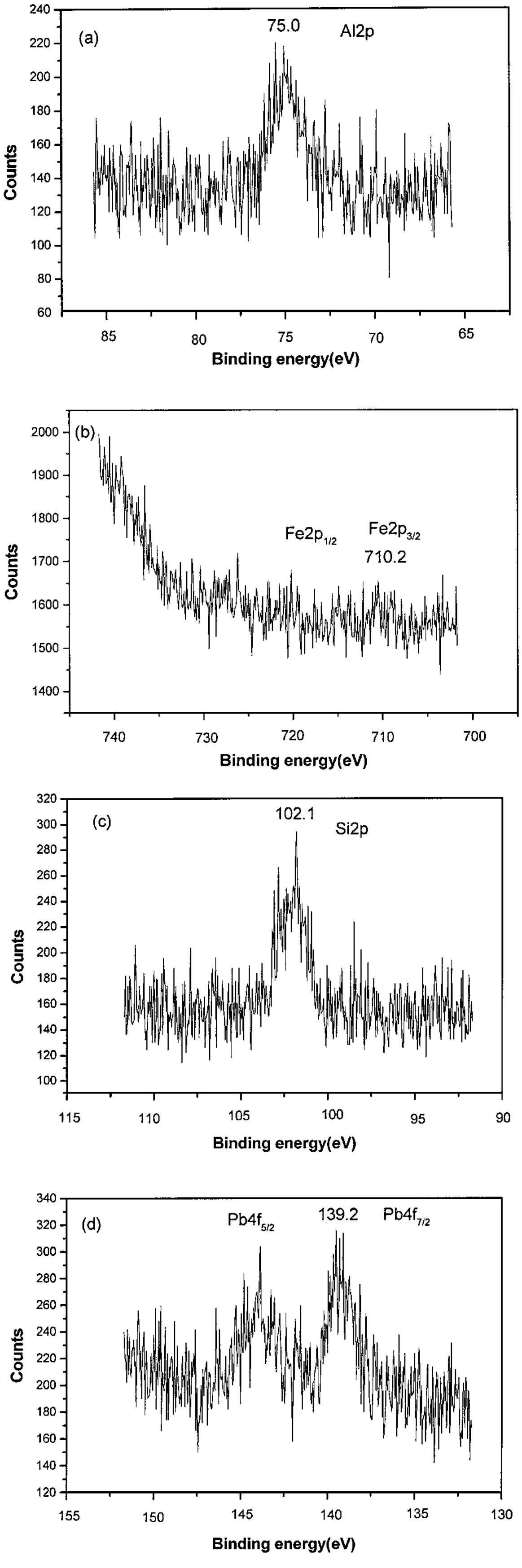

Figure 7 XPS spectra of a worn surface of Al-4Si-1Cu-20Pb at a load of 200 N: (a) Al 2p, (b) Fe $2p_{3/2}$, (c) Si 2p, and (d) Pb $4f_{7/2}$.

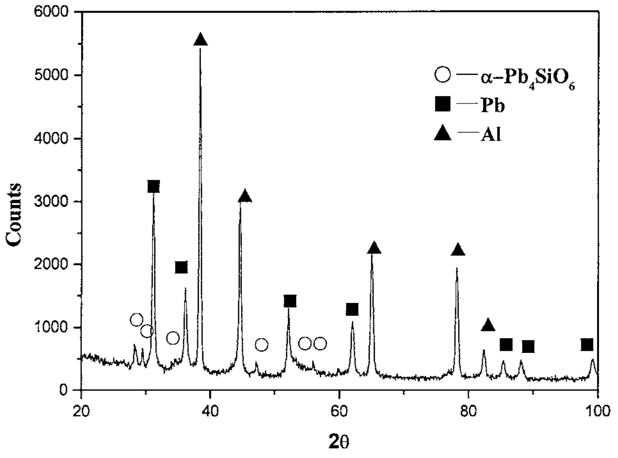

Figure 8 XRD analysis of the wear debris of hot extruded Al-4Si-1Cu-20Pb at 200 N.

TABLE IV The composition of worn and unworn surface of Al-4Si-1Cu-20Pb at 200 N, at%

Element	Unworn surface	Worn surface
O	46.40	54.68
Al	35.26	23.53
Si	15.67	15.96
Cu	0.18	0.28
Pb	2.37	5.33
Fe	0.11	0.22

a certain kind of silicate in which silicon and lead exist. One possible silicate may be alpha lead silicate (Pb_4SiO_6). In Fig. 8, the XRD analysis of wear debris generated under the same experimental condition dry sliding indicates that they contain Pb_4SiO_6, which is certainly a constituent of the black film of lubricant. Others also have found this constituent in the wear debris of Al-Pb alloys at the similar load level [8]. These results indicate that the film of lubricant actually is a reacted one, and it is not a lead film as it has been assumed by many workers [1, 2–8]. The SEM micrograph of the subsurface and the corresponding Al, O, and Pb dot-map images in Fig. 9, show the reacted film at the surface of the worn pin of the Al-4Si-1Cu-20Pb and the evidence of plastic flow below the surface. The surface composition obtained by XPS analysis of the worn and unworn surface of Al-4Si-1Cu-20Pb specimen as shown in Table IV also reflected the enhanced concentration of O and Pb after the formation of reacted film. Based on the above results, the formation mechanism of the lead-rich reacted film is proposed to be two consecutive processes: first, during the start of running-in wear the relatively hard and strong matrix of the bearing alloy is forced deeper, caused by extrusion and smearing of the lead over the surface of the test pin. In the next few runs, a uniform film of smeared lead is formed over almost the entire pin surface; this process has been assumed by many workers [7–11]. Then, the lead, aluminum, silicon on the surface reacted with oxygen in atmosphere and amongst each other under high contact pressure and surface temperature. The results in this paper revealed that no pure lead was found in the film, lead existed in the form of compound and became an effective constituent of mixed lubricating film. This may be attributed to the friction heating at higher load than that previously applied on as cast Al-Pb alloys by other workers [7–11].

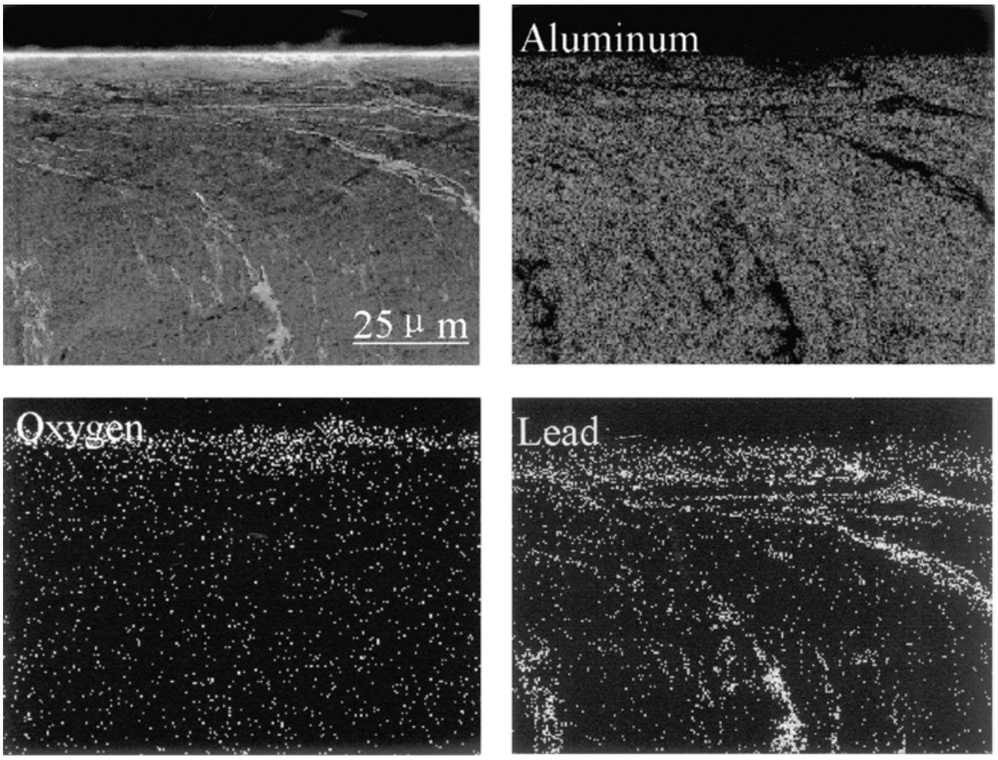

Figure 9 The SEM micrograph of the transverse section of the worn surface and corresponding Al, O, and Pb dot-map images.

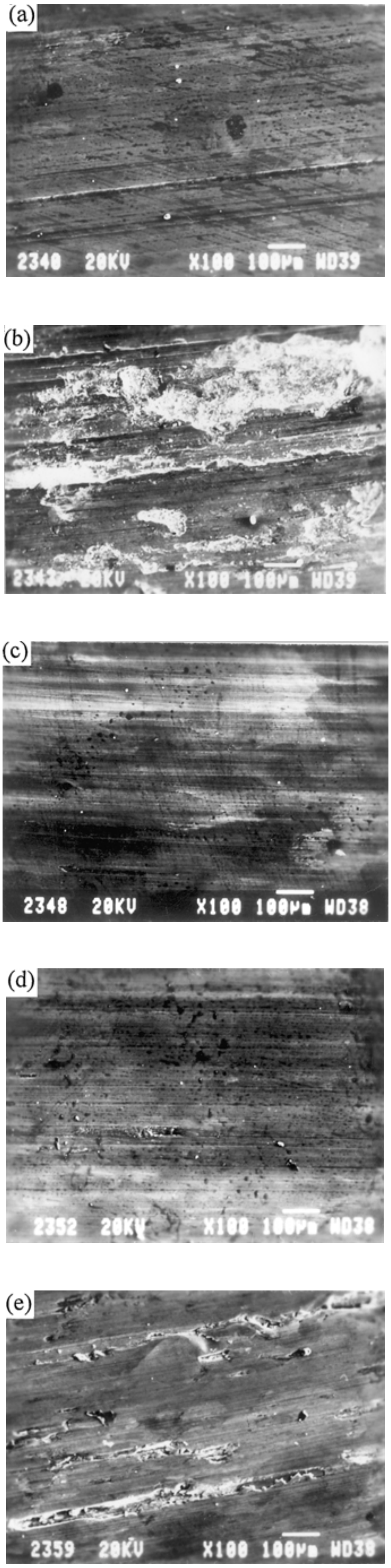

Figure 10 Worn surfaces of the Al-4Si-1Cu-20Pb at different applied loads of (a) 60 N, (b) 140 N, (c) 200 N, (d) 240 N, (e) 280 N and (f) a crack in subsurface at 280 N. (*continued*)

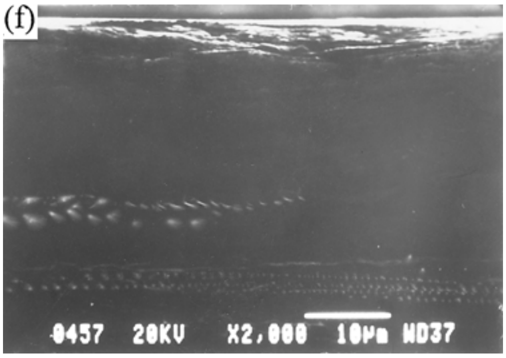

Figure 10 (*continued*).

3.4. Analysis of anti-seizure behavior of the reacted film

The worn surfaces of Al-4Si-1Cu-20Pb alloy pins at various loads are shown in Fig. 10. Before the load has reached the plateau range, the worn surfaces appear rather rough. But the worn surface becomes smooth owing to formation of the compact reacted film covering almost the entire surface when the load is increased to enter the plateau range. Before the seizure deep craters clearly appeared on the worn surface and the SEM image of the subsurface in the transverse section under the surface shows the formation of crack, indicating that the crack initiation and growth take place mainly in subsurface. Thus, delamination wear is the main mechanism. The wear rate in this region increases very slowly with the applied load, and almost displays a plateau. This phenomenon has also been observed in the SiC particle-reinforced A356 and spray deposited AlCuMn alloy [21]. The reason is that the propagation of subsurface crack needs to meet a certain stress condition, and the crack can keep relative stability in a certain load range, resulting in a relative stable wear rate. To understand the seizure mechanism the worn surfaces at different distance of sliding under limit load for seizure have been examined in Fig. 11, before seizure occurred. Scratches being to appear on certain regions locally, then the area increased until the occurrence of seizure. The worn surface shows a lot of cracks in the rough region where a large amount of material transfer from the pin to the disc has occurred.

It is well known that the seizure is generally caused by high unit loading, leading to surface rupture, penetration and removal of surface layer from at least one of the mating surfaces. It appears that such a mechanism controls the seizure as observed in the present investigation. The reacted films formed under high applied loads and high temperatures are stable and have good bonding with the alloy underneath as shown in Fig. 9. Constituents of the reacted films, which are nonmetallic, have poor adhesion with the mating surface. These films at the interface of mating surfaces keep a nonmetal-metal contact, and hence, the resistance to wear and friction including anti-seizure property is improved. It should be noted that the lead content of the alloy plays a much more significant role than other elements in lowing the friction and preventing seizure.

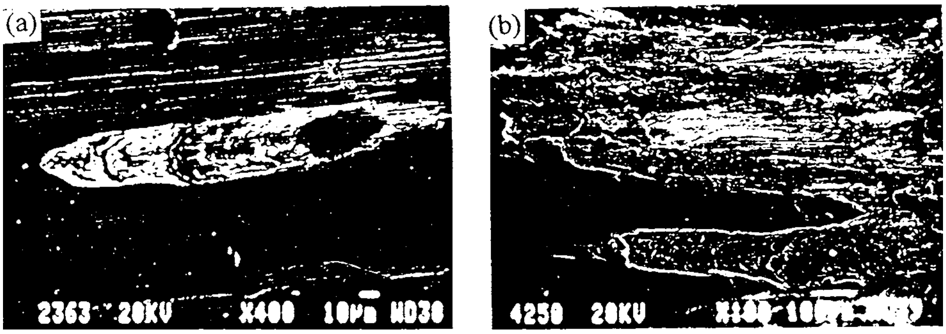

Figure 11 The worn surface of the Al-4Si-1Cu-20Pb at the seizure load of 300 N, (a) after sliding through a distance of 94.2 m and (b) sliding through a distance of 244.9 m (with seizure occurring).

4. Conclusions

The present study on the role of the reacted film of AlSiCuPb alloys in enhancing anti-seizure property leads to the following conclusions.

1. Hot extruded AlSiCuPb alloys containing 20 wt% and 25 wt% lead have better characteristics of friction and wear than those in the base alloy without lead. The wear rate and coefficient of friction in AlSiPb alloys decreases with increasing lead content, and especially, the anti-seizure property of AlSiPb alloys containing 20 wt% and 25 wt% lead have improved remarkably.
2. In a higher load range, the stable wear rate and the lowest coefficient of friction before seizure have resulted from the formation of a reacted film on the worn surface.
3. The reacted film has significant effect on decreasing the wear rate and increasing the anti seizure property. This film is a mixture of different compounds containing Al, Fe, Si, O and Pb.

Acknowledgements

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