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The aluminium–silicon system to 5.5 GPa

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Abstract. The influence of pressure on the phase relations in the Al–Si system has been studied to 5.5 GPa. The eutectic temperature passes through a maximum at 3.95 GPa, 626 °C; this is similar to the behaviour reported previously for the Al–Ge system. The experimentally determined data are in disagreement with theoretically calculated phase behaviour for the system.

1 Introduction

The Al–Si composition–temperature phase diagram is a simple eutectic system with limited solid solubility at atmospheric pressure (Hansen and Anderko 1958; Elliot 1965; Shunk 1969) (figure 1). The eutectic is located at 12.3 at% silicon and at 577 °C. The Al–Si system is of importance for lightweight alloys, particularly in motor car engines (Hellawell 1970).
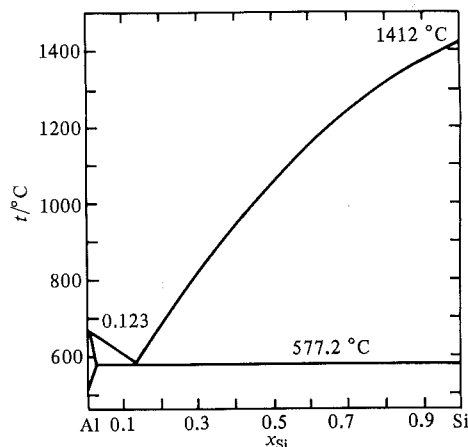

Figure 1. The Al–Si composition–temperature phase diagram (Hansen and Anderko 1958).
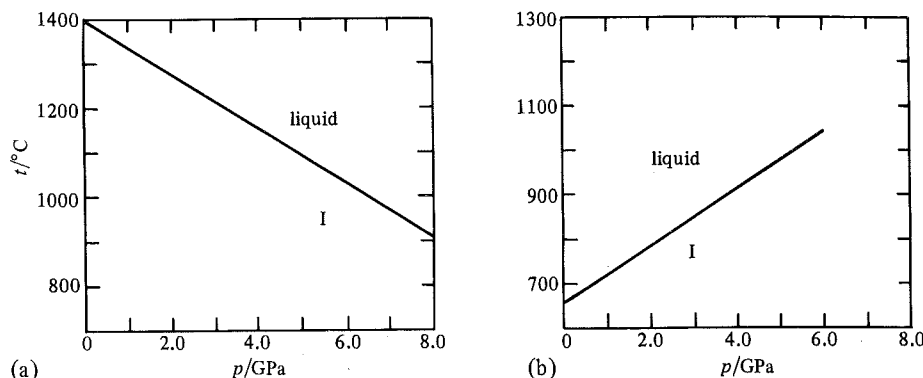

Figure 2. The influence of pressure on the melting points of the endmembers in the Al–Si system (Cannon 1974; Pistorius 1976): (a) silicon; (b) aluminium.

The influence of pressure on the melting points of the end members (Cannon 1974; Pistorius 1976) is shown in figure 2. Chernov and Shinyaev (1974) have calculated the effect of high pressures (up to 5.6 GPa) on the Al–Si system. Mii et al (1976) have studied the low-Si region of the composition–temperature phase diagram, and have determined the effect of pressures of 2.8 and 5.4 GPa on the system. The phase boundaries were detected by means of resistance measurements. In addition, Banova et al (1979) have drawn certain parallels between the Al–Si system and the Al–Ge system at high pressures.

The aim of the present study is to determine the phase relations for the Al–Si system at pressures of up to 5.5 GPa and high temperatures, with particular reference to the appearance of new stable phases and variations in composition as a function of pressure.

2 Experimental

Pressures were generated in a piston–cylinder device (Kennedy and La Mori 1961). Thermal events under high pressure were studied by differential thermal analysis (DTA), with Chromel/Alumel thermocouples. The detailed experimental procedure has been described elsewhere (Pistorius and Clark 1969; Richter et al 1978). The samples were contained in modified niobium capsules (Clark et al, to be published). Stainless steel capsules were also tried. Analysis by scanning electron microscopy (SEM) revealed that contamination occurred in the stainless steel capsules, but niobium capsules showed no contamination as long as temperatures in excess of the liquidus temperature were not maintained for lengthy periods (less than a few minutes). Thermal overshoot into the liquid region was kept to a minimum and all capsules were subjected to post-experimental SEM analysis. Results quoted are for samples free from contamination. Heating/cooling rates varied from 0.4 to 0.8 °C s^{-1}. Typical DTA signals for solidus and liquidus temperatures are shown in figure 3. Only melting temperatures were plotted, and the final data are believed to be correct to within ±1 °C and ±0.5 GPa.

Alloy compositions were prepared from aluminium rod with a stated purity of 99.999% from Koch-Light Laboratories, and from single-crystal silicon (semiconductor grade) from Wacker Chemitronic GmbH which was better than 99.99% pure. The high vapour pressure of aluminium at its melting temperature made alloy preparation
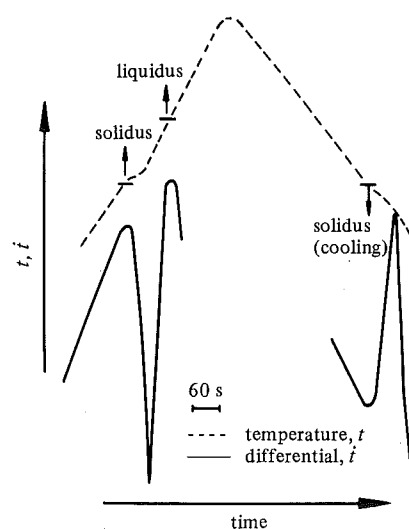
Figure 3. Typical DTA signals obtained for the solidus and liquidus boundaries at 1.04 GPa.

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Figure 4. The effect o

difficult at atmospheric pressure. Several methods were tested, but the only satisfactory one was an in situ reaction: that is, the correct amounts of aluminium and silicon were weighed and loaded directly into a high-pressure DTA capsule. The capsule was sealed and placed in the pressure vessel, the pressure was raised to 0.8 GPa, and the temperature was then raised to above the aluminium melting point for 15 min. Finally, the alloys were annealed at just above the eutectic temperature for several hours.

3 Results and discussion

Differential scanning calorimetry (DSC) analyses were performed on the samples at atmospheric pressure after the high-pressure experiments. These yielded a eutectic temperature of 574 °C, in reasonable agreement with the published value of 577 °C (Meussner 1959). The liquidus values were difficult to determine by DSC at atmospheric pressure, but the values obtained agreed with published data on the composition–temperature diagram (Hansen and Anderko 1958; Elliot 1965; Shunk 1969).

The effect of pressure on the eutectic temperature is shown in figure 4. The eutectic temperature, t_E, rises with pressure with an initial slope of 26 °C GPa^{-1}, passing through a broad maximum at 3.95 GPa, 626 °C, after which it falls with increasing pressure. The experimental points could be fitted by the equation

$$t_E/°C = 574.7 + 25.92(p/GPa) - 3.27(p/GPa)^2,$$

with a standard deviation of 1.1 °C.

Cooling signals coincided exactly with the heating signals up to the solidus maximum. Thereafter, thermal hysteresis increased with increasing pressure, as shown in figure 4. These signals showed a significantly larger scatter than the heating signals. The same behaviour was observed in the Al–Ge system (Clark and Pistorius 1974).

In order to study the effect of pressure on composition, an off-eutectic alloy composition was selected (Al–13.5 wt% Si). The data obtained for this composition are presented in figure 5.

No liquidus signals could be observed at pressures up to 0.4 GPa. Thereafter the liquidus was observed and was found to increase with increasing pressure, as shown in figure 5. A tentative boundary is shown in the figure for the liquidus up to 0.4 GPa.

The data indicate a shift in the eutectic composition to higher silicon content with increasing pressure. At 0.4 GPa, 586 °C, therefore, the eutectic composition lies at 13.5 wt% silicon. This is in good agreement with values expected from Mii et al (1976).
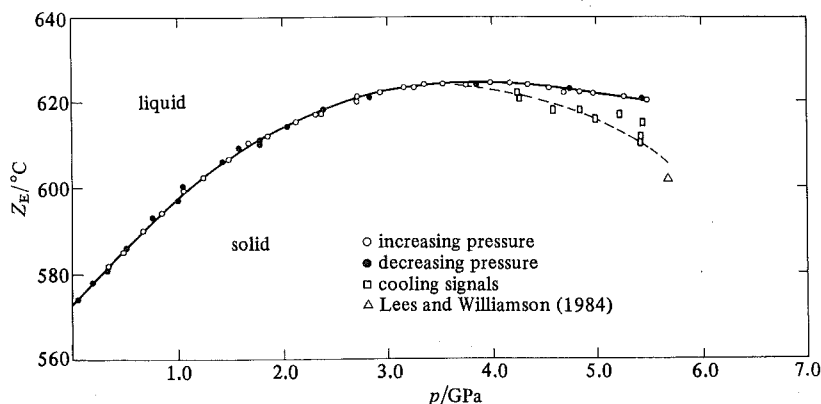

Figure 4. The effect of pressure on the Al–Si eutectic temperatue, t_E.

Figure 6 shows a comparison of the present data with those of Chernov and Shinyaev (1974) for Al–13.5 wt% Si. Agreement with the calculated liquidus data of Chernov and Shinyaev is fairly good, but their data do not predict a maximum for the solidus. In this regard it is worthwhile to compare the Al–Si system with the Al–Ge system. Germanium, like silicon, also shows a decrease in melting temperature with increasing pressure. The Al–Ge eutectic temperature also increases initially with pressure, passes through a broad maximum at ~1.39 GPa, 420.7 °C, and then falls with further pressure increase. In addition, extrapolation of the data of Mii et al (1976) also suggests a maximum in the eutectic temperature at high pressure.

In the case of the Al–Ge system, a calculated phase diagram up to 2.0 GPa has also been published (Banova et al 1979). Once again, the eutectic composition is predicted to shift away from the high aluminium content with increasing pressure. The calculated effect of pressure on the eutectic temperature up to 2.0 GPa is shown in figure 7, and compared with the Clark and Pistorius (1974) data. The similarities with the Al–Si system are apparent, and it can therefore be concluded that the models used by Chernov and Shinyaev (1974) and Banova et al (1979) are insensitive to the processes which cause the eutectic temperature to pass through a maximum. The models need to build in a component of the 'two-species' model used by Rapoport (1967) to describe melting-curve maxima in pure compounds.
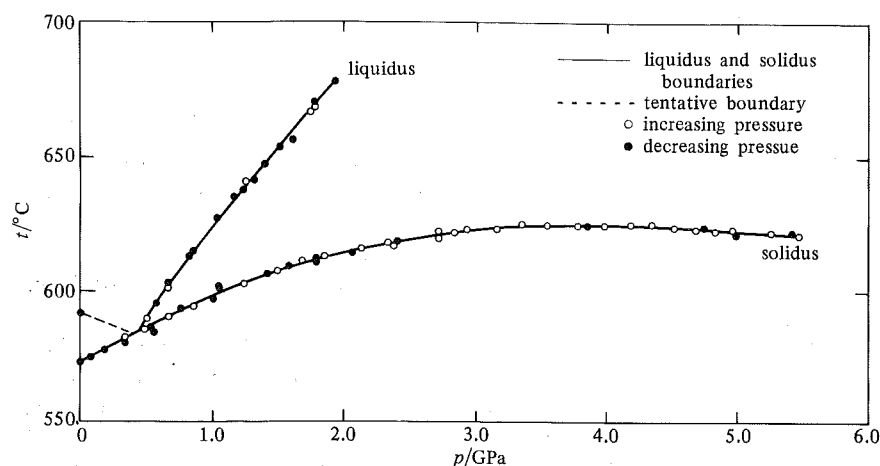
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Figure 7. Comparison

Table 1. Phase relation

$t_E(p)$	$t_E/°C$
	3.2
t_E^{max}	3.95
Initial slope, dt_E/dp	25.9

[a]Mii et al (1976).

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Figure 5. The temperature–pressure phase diagram of Al–13.5 wt% Si.

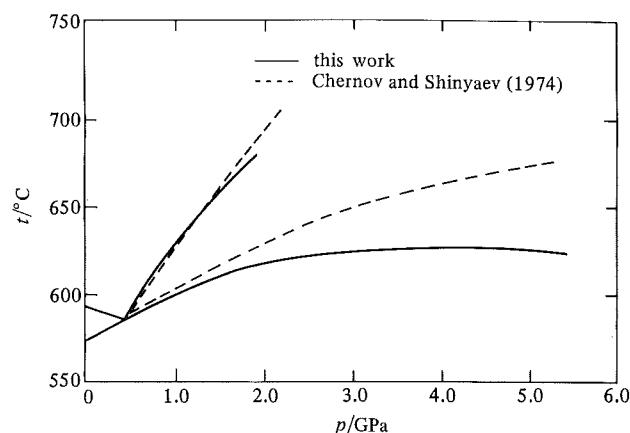**Figure 6.** Comparison of present data for Al–13.5 wt% Si as a function of pressure with those from the literature.

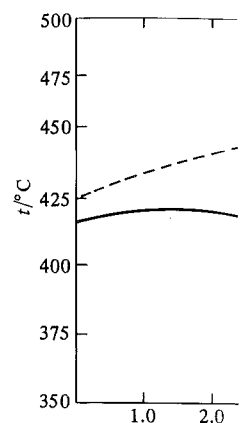The solidus phase relations of Al–Si as a function of pressure, together with those of Al–Ge, are summarized in table 1.
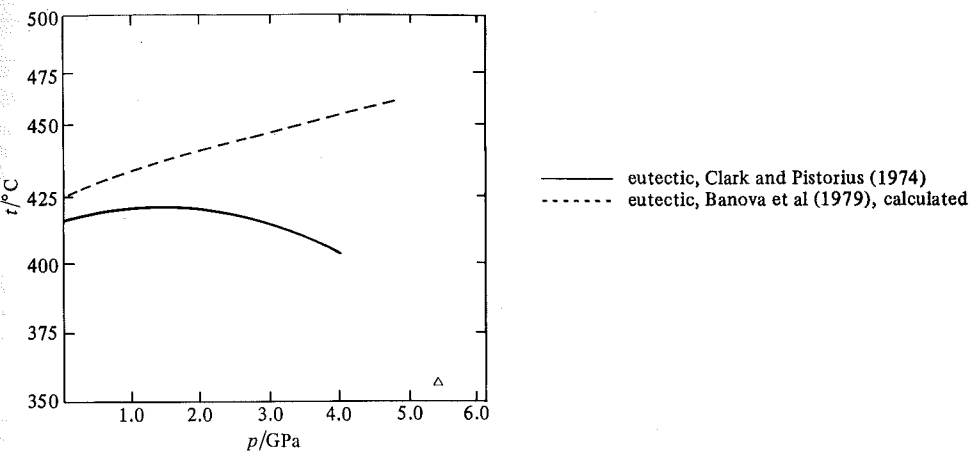

Figure 7. Comparison of data for the Al–Ge eutectic temperature as a function of pressure.

Table 1. Phase relations for Al–Si and Al–Ge.

	Al–Si	Al–Ge [a]
$t_E(p)$	$t_E/°C = 574.7 + 25.92(p/\text{GPa}) - 3.27(p/\text{GPa})^2$	$t_E/°C = 415.5 + 7.5(p/\text{GPa}) - 2.7(p/\text{GPa})^2$
t_E^{max}	3.95 GPa; 626 °C	1.39 GPa; 421 °C
Initial slope, dt_E/dp	25.9 °C GPa^{-1}	7.5 °C GPa^{-1}

[a]Mii et al (1976).

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