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The microstructural control of cast and mechanical properties of zinc–aluminium alloys

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The zinc–aluminium alloys containing 8, 12, and 27% aluminium are finding increasing applications in the casting industry. These alloys are stronger than most aluminium alloys. In addition, they possess high wear resistance and bearing properties. However, surface sinks and shrinkage defects are observed on the bottom faces of such castings, contrary to general foundry practice. In the present investigation, this problem observed in the Zn–8% Al, Zn–12% Al, Zn–27% Al alloys was tackled by controlling various casting parameters and also by additions of the master alloys of strontium and lithium into the molten alloys. It was found that the underside shrinkage problem was influenced by the aluminium content of the alloy, melt superheat, casting size and cooling conditions. The strontium and lithium additions were found to be beneficial in reducing the underside shrinkage problem. The ultimate tensile strength, fracture elongation and Vickers hardness were all increased with aluminium concentration and lithium addition. It was found also that the most problematical Zn–27% Al alloy, which provided the highest mechanical properties, was very suitable for the squeeze-casting technique. The mechanical properties were increased sharply in these squeeze-cast bars.

1. Introduction

Zinc has been used traditionally to galvanize steel surfaces against corrosion. Since the 1930s, die-cast zinc alloys also have been in use. Zinc–aluminium alloys, however, as general-purpose castings, appeared more recently. The Zn–8% Al (ZA-8), Zn–12% Al (ZA-12) and Zn–27% Al (ZA-27) casting alloys have been developed primarily in North America and are finding increasingly wide applications [1–3]. The exact chemical compositions of the three commercial alloys are defined in ASTM B669-84.

These alloys in general are stronger than most aluminium alloys and possess high bearing properties. In spite of their advantages and promise, however, they suffer surface sinks and shrinkage defects at the bottom faces of the castings, contrary to general foundry practice. This behaviour, i.e. the so-called underside shrinkage problem, develops most seriously in the Zn–27% Al castings which usually show the best mechanical and physical properties among the three alloys. To date, the origins of the underside shrinkage problem and its probable remedies have been researched mostly in Canada [4–7]. It has been noted that the underside shrinkage problem arises primarily due to the long freezing ranges and the density differences occurring between the solidified alloy and its melt during freezing. The underside shrinkage problem could be prevented in the Zn–8% Al and Zn–12% Al alloys by adjusting the casting size and casting parameters. Sahoo *et al.* [7] reported that strontium additions below 0.06% Sr also relieved the same problem in the Zn–27% Al alloys [7].

The purpose of the present investigation was to prevent the underside shrinkage problem without degrading the mechanical properties of these alloys. The experimental work was carried out in three stages:

(i) First, the effects of alloy composition and casting parameters were studied on both underside shrinkage behaviour and mechanical properties.

(ii) Then, the effects of strontium and lithium additions were determined on the most problematical Zn–27% Al castings.

(iii) The cast quality and mechanical properties of the Zn–27% Al alloy as a result of squeeze-casting were also examined.

2. Experimental procedure

2.1. Materials and moulds used

The three zinc–aluminium alloys were prepared using 99.995% Zn and 99.7% Al metals. The master alloys available were Al–9.6% Sr and Al–10% Li. To increase the surface quality of the castings a fine-grain sand was used for the sand moulds. These moulds were of 3.0 in. (76.2 mm) diameter and of various heights as given in Table I. To examine its bottom shrinkage behaviour more closely a 1.50 in. (38.1 mm) high additional sand mould was also prepared for the Zn–27% Al (ZA-27) alloy. A split squeeze-casting die and its punch were machined from mild steel. The diameter and the height of the die cavity were respectively 7.5 and 135 mm.

TABLE I Mould height, melt superheat, and strontium and lithium additions for zinc-aluminium castings

Mould height		Melt superheat (°C)				
in.	mm	ZA-8	ZA-12	ZA-27	ZA-27 + 0.05% Sr	ZA-27 + 0.1% Li
0.33	8.4	100	100	100	–	–
0.50	12.7	100	100	100	100	–
1.00	25.4	100	100	100	100, 150	150
1.50	38.1	–	–	150	–	–
2.00	50.8	100	100	100	–	–

2.2. Casting practice

As seen in Table I, the size of the sand castings was controlled by varying the mould height. Castings into these moulds were usually made using a 100 °C melt superheat. The Zn–27% Al alloy was also cast with a 150 °C melt superheat to exaggerate the underside shrinkage problem. The strontium and lithium master alloys were stirred into the molten Zn–27% Al alloys under an argon atmosphere shortly before casting. The tension test bars were cast separately, both into sand moulds at room temperature (20 °C) and into graphite moulds preheated to 350 °C. The surface roughness at the bottom face of a cylindrical casting was measured when it was possible.

To prevent premature freezing an ample time should be ensured during squeezing the semi-solid alloy. In the present experiments, before a squeeze-casting run the Zn–27% Al melt was kept in a furnace at 700 °C whilst the die and its punch were kept in a second furnace at 500 °C. First, the die was removed from its furnace and placed in a hydraulic press. Following this the molten Zn–27% Al alloy was poured into the die cavity. Finally, the punch was taken from the furnace and was placed in its position as soon as the freezing started. A 15 kN compressive force, which corresponded to 80 MPa pressure [8], was delivered on to the freezing alloy until the temperature dropped below the solidus curve.

2.3. Metallography and tension test practice

All the cylindrical castings were sectioned in their transverse and longitudinal directions for metallographic examination. The tension test samples were machined from the cast bars according to the ASTM E8 standard. These samples were pulled and fractured in an Instron 1186 universal tension test machine. Metallographic specimens were cut off from the bottom quarters of these fractured samples. The fracture surfaces of the squeeze-cast Zn–27% Al bars were examined in a Jeol JSM T300 SEM.

3. Results and discussion

3.1. Cast quality

The effects of alloy composition, melt superheat and cast height on sinks and shrinkages formed at the bottom faces of the cylindrical castings are summarized in Table II. As mentioned already, these problems increased with the aluminium content and became most serious in the Zn–27% Al alloy. The melt superheat was found to be more influential than the casting size in the present results. In fact by lowering the melt superheat to 50 °C the sinks and shrinkages formed at the bottom faces could be prevented completely in the Zn–8% Al and Zn–12% Al castings. The surface roughness values measured were found to range from 15 to 30 μm on these faces.

The same measurements, however, were not made on the Zn–27% Al castings due to the excessive roughness appearing at their bottom faces. Here, it was also noted that the melt superheat was more effective in increasing the problem. The bottom faces of the larger castings, i.e. 1.5 in. (38.1 mm) and 2.0 in. (50.8 mm) high cylinders, sank completely and rather large shrinkage cavities were developed when the melt was cast with 150 °C superheat.

As noted in Table I, strontium and lithium were added only to the most problematical Zn–27% Al castings. Following the suggestion of Sahoo *et al.* [7] the strontium concentration was kept at 0.05% Sr to prevent the formation of a strontium-containing intermetallic phase. Lithium, however, has considerable

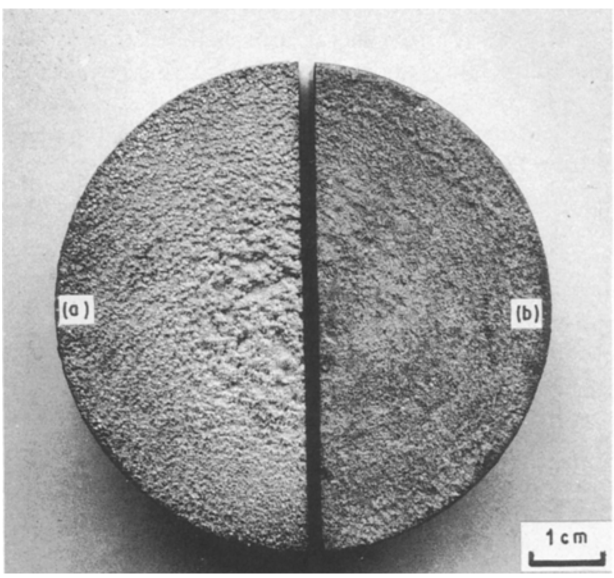

Figure 1 The two halves of bottom faces of two 1.0 in. (25.4 mm) high cylinders cast with 100 °C melt superheat: (a) strontium-free half, (b) 0.05% Sr added half.

TABLE II Effects of alloy composition, melt superheat and cast height on the sinks and shrinkages formed at the bottom faces of cylindrical castings

Alloy	Melt superheat (°C)	Cast height (in.)[a]	Surface sink	Underside shrinkage
ZA-8	50	1/3	None	None
		1/2	None	None
		1	None	None
		2	None	None
	100	1/3	None	None
		1/2	None	None
		1	None	Microshrinkage pores
		2	None	Microshrinkage pores
ZA-12	50	1/3	None	None
		1/2	None	None
		1	None	None
		2	None	None
	100	1/3	None	None
		1/2	None	None
		1	None	Microshrinkage pores
		2	Local sink at centre	Microshrinkage pores
ZA-27	50	1/3	None	Very few
		1/2	None	Very few
		1	None	Very few
		3/2	None	Very few
		2	None	Very few
	100	1/3	None	Very few
		1/2	None	Few
		1	None	Moderate
		3/2	Complete sink	High
		2	Complete sink	High
	150	1/3	None	Few
		1/2	None	Moderate
		1	None	High
		3/2	Complete sink	High
		2	Complete sink	Very high

[a] 1 in. = 25.4 mm.

solid solubility in aluminium, so its added concentration was doubled and increased to 0.1% Li. It was found that both strontium and lithium additions reduced significantly the sinks and shrinkages formed at the bottom faces of the Zn–27% Al castings. The situation for two of these cylindrical castings is illustrated in Fig. 1. The improvement following strontium addition is evident in Fig. 1b. As a result, surface roughness measurements could be made and found to vary between 25 and 35 μm to the bottom faces of strontium- and lithium-added cylindrical castings.

The tension test bars were small enough not to suffer the sinks and shrinkages mentioned above. The squeeze-cast samples possessed the best surface quality among all cast bars.

3.2. Microstructure

Zn–8% Al and Zn–12% Al are hypereutectic alloys whereas the freezing of Zn–27% Al alloy also involves a peritectic reaction before eutectic freezing. All three alloys are rich in aluminium, which appears as dendrites embedded in the microstructure. The amount of aluminium-rich phase increases with the aluminium content. Fig. 2a is a micrograph of a Zn–27% Al alloy cast into the mild steel squeeze-casting die preheated to 500 °C and then solidified freely without application of pressure. In this micrograph the large, columnar aluminium-rich dendrites appear white and the eutectic is grey in colour. The small, very dark spots are interdendritic shrinkage microporosities, characteristic of long freezing-range alloys. It is noted that the branches of aluminium-rich dendrites are enclosed in a grey, zinc-rich skin which is an indication of the incomplete peritectic reaction. The coring effects revealed by colour variations in these dendrites are also typical of a long freezing-range alloy.

The microstructure of the same alloy which was squeezed in the same die under 80 MPa pressure during its freezing is shown in Fig. 2b. This is a significantly different picture; the amount of aluminium-rich dendrites increased significantly at the expense of the eutectic phase and the microporosities in the microstructure. The density of this particular casting is 5.42 g cm^{-3}, i.e. a 9% increase as compared with Fig. 2a. In the squeeze-casting process the applied pressure forces the melt or the semi-solid metal to flow into the probable shrinkage regions to prevent porosities from forming. Hence, a long freezing-range alloy accommodates such a form of melt flow easily, resulting in a sound casting with a relatively small applied pressure [8, 9].

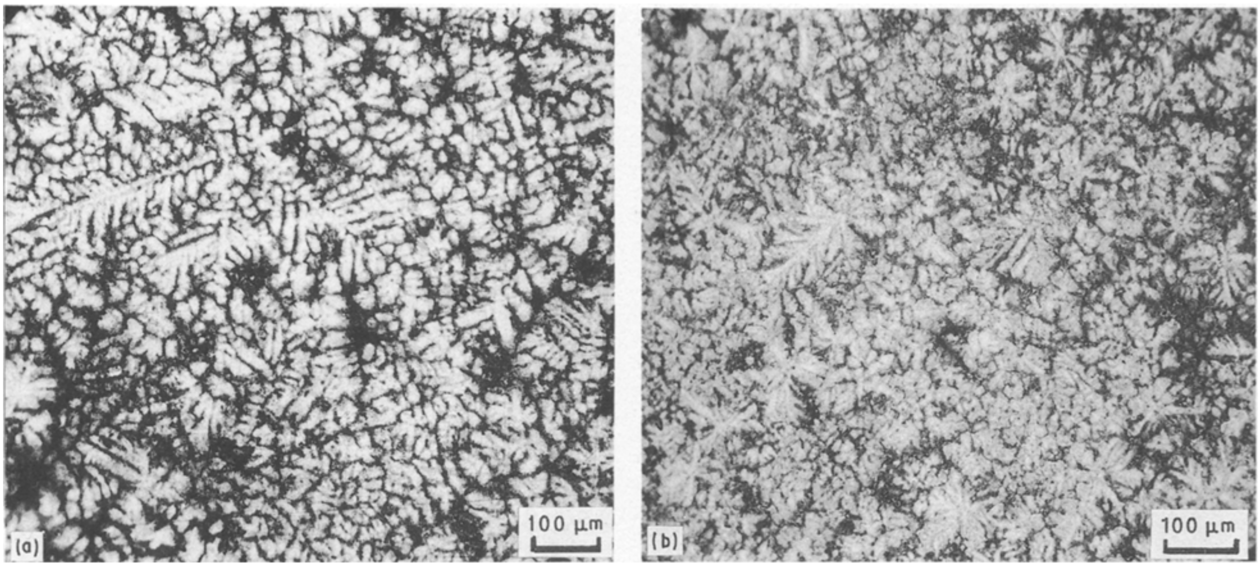

Figure 2 The microstructures of ZA-27 alloy cast into the same mild steel squeeze-casting die preheated to 500 °C: (a) not squeezed, (b) squeezed under 80 MPa.

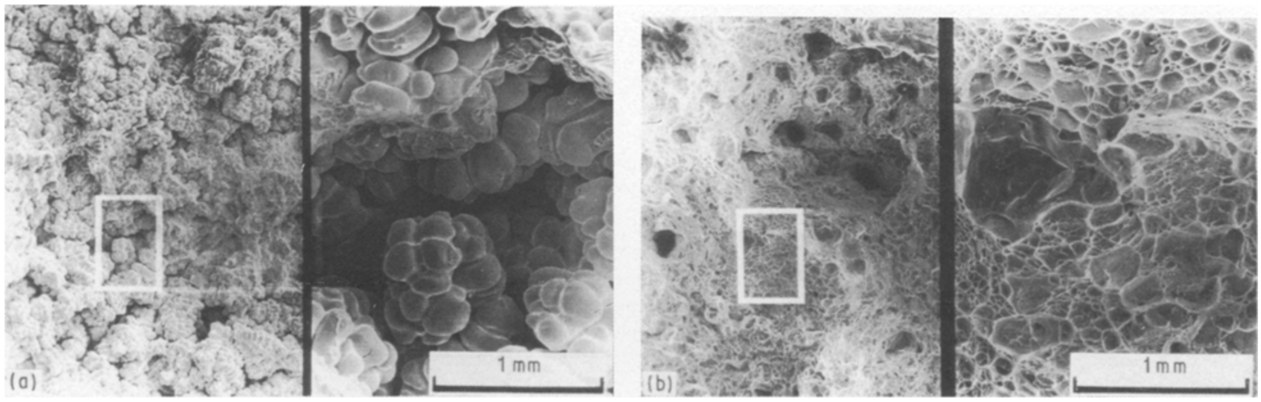

Figure 3 SEM micrographs of tension-test fracture surfaces found in ZA-27 cast bars: (a) not squeezed, (b) squeezed under 80 MPa.

TABLE III Typical secondary dendrite arm spacings (µm) in various moulds

Alloy	Moulds		Mild steel die		
	Graphite (350 °C)	Sand (25 °C)	500 °C	500 °C casting squeezed under 80 MPa	350 °C
ZA-8	6	15	–	–	–
ZA-12	7	25	–	–	–
ZA-27	18	25	68	28	20

The microstructures of the tension test bars were analysed by measuring the secondary dendrite arm spacings (SDAS) of the aluminium-rich phase in all alloys. As seen in Table III, the SDAS values increased with the aluminium content of the alloys. Although they were not preheated, the sand-mould castings resulted in coarser SDAS than their graphite-mould counterparts.

As given in Table III the SDAS in the squeeze-cast microstructure of Fig. 2b is 28 µm as compared with 68 µm for the unsqueezed casting of Fig. 2a. This should arise primarily from increased heat transfer and heterogeneous nucleation rates during squeezing [9]. The SDAS value is reduced more effectively when the alloy is cast into a cooler die. The same mild steel die preheated to only 350 °C produced a 20 µm SDAS value. Squeezing also reduced the interdendritic microporosity as mentioned above. Another feature noted in Fig. 2b is that the microsegregation inside the dendrites is not relieved by squeeze casting. This problem can be eliminated, however, by a proper heat treatment [8].

Fig. 3a shows the tension test fracture surface of the sample seen in Fig. 2a. It is understood that this sample fractured interdendritically; hence it is possible to identify each dendrite present at the fracture surface. Fig. 3b corresponds to Fig. 2b and reveals a transdendritic, ductile fracture behaviour. Squeeze-casting apparently reduces the interdendritic microporosity and interlocks the dendrites. It is noted, however, that some microporosity is still left after the squeeze-casting process.

The microstructures of cylindrical castings were examined in their transverse and longitudinal directions. Particularly in the Zn–27% Al castings, it was noticed that the top and the side regions contained more aluminium-rich dendrites than the bottom and the inner regions. This anisotropy in the microstructure also introduced variations in hardness of the castings, as seen in Table V below.

TABLE IV Effects of squeeze-casting on ultimate tensile strength (σ_{ULT}) and fracture elongation (ε_f) of ZA–27 alloy

Die and punch temp. (°C)	Cast No.	σ_{ULT} (MPa)	ε_f (%)
Not squeezed			
500	1	263	2.5
	2	317	4.7
350	3	444	6.0
	4	538	7.8
	5	417	7.4
Squeezed			
500	6	519	8.9
	7	631	14.9
	8	522	9.5
	9	700	16.2

TABLE V Effects of strontium and lithium on the variation of hardness in 1.00 in. (25.4 mm) high cylinders cast with 100 °C superheat

	Vickers hardness	
Alloy	Sectioned surface	Outside surface
ZA–27	88.5	90.8
	77.2	92.4
	68.1	94.2
	47.5	94.1
	38.1	85.4
	39.9	61.3
	Average: 59.9 VH	Average: 86.4 VH
ZA–27 + 0.05% Sr	74.2	91.6
	64.8	94.9
	70.7	74.1
	79.8	89.2
	93.6	98.1
	71.9	89.2
	Average: 75.8 VH	Average: 89.5 VH
ZA–27 + 0.1% Li	97.5	120.7
	97.5	120.7
	115.9	119.1
	115.9	120.7
	125.1	115.6
	110.3	120.5
	Average: 110.4 VH	Average: 119.5 VH

3.3. Mechanical properties

3.3.1. Tensile properties

The results of the tensile tests can be summarized into two separate groups as given in Fig. 4 and Table IV. In Fig. 4 it is found that the ultimate tensile strengths and fracture elongations of the cast bars increase with the aluminium content of the alloys, i.e. with the aluminium-rich dendrites. It is noted that while the fracture elongations of sand-cast bars here are above those values given in the literature [1], the tensile strength values are below their counterparts reported in the same literature. Such a difference should be anticipated, since the literature values were obtained using commercial alloys which contain copper and magnesium to increase their strength at the expense of ductility.

A second feature of Fig. 4 in conjunction with Table III is that the graphite-cast bars which have smaller SDAS values, resulting in lower tensile properties than the sand-cast bars. This is, however, contrary to the usual expectations. Hence, factors other than the SDAS should be more important in determining the tensile properties. It is noteworthy that Barnhurst and Gervais [5] also found that the SDAS did not markedly influence the tensile properties of these alloys.

As mentioned earlier, strontium and lithium additions to the most problematical Zn–27% Al alloy were made to reduce the underside shrinkage problem. Nevertheless, this should not be achieved at the expense of tensile properties. However, the ultimate tensile strength of both sand- and graphite-cast bars were reduced significantly, i.e. dropped by approximately 30 MPa, upon 0.05% Sr addition. This behaviour is attributed to the fact that this strontium level would be too close to its upper limit of 0.06% Sr, so that a strontium-containing intermetallic would form in the microstructure [7]. In contrast, lithium does not degrade but slightly improves the ultimate tensile strength. In fact, due its considerable solid solubility in aluminium, lithium solution hardens the aluminium-rich dendrites. The large increase in hardness of the same alloy given in Table V below is presumably a result of this effect.

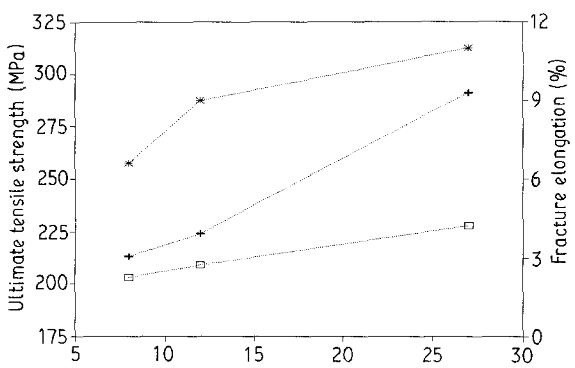

Figure 4 Ultimate tensile strength (σ_{ULT}) and fracture elongation (ε_f) versus Zn–Al alloy composition in sand- and graphite-cast bars: (□) UTS (graphite-cast), (+) UTS (sand-cast), (∗) fracture elongation (sand-cast).

The effects of die temperature and squeeze-casting on the tensile properties of Zn–27% Al cast bars are summarized in Table IV. It is seen that in the unsqueezed castings the tensile properties are influenced by the die and punch temperature. Hence, after reducing their temperature from 500 to 350 °C the σ_{ULT} and ε_f values of the cast bars increased. The data obtained here cannot be directly compared with those of Fig. 4 or those in the literature [1]. Nevertheless, the advantages of reduced die temperature and squeezing are evident. In both situations higher σ_{ULT} and ε_f values are reached as compared to the literature values [1]. Squeeze-casting provided remarkable increases both in σ_{ULT} and ε_f. As can be seen in Table IV, when the die temperature is fixed at 500 °C, squeeze-casting briefly doubles σ_{ULT} and triples ε_f values. It is understood that even higher σ_{ULT} and ε_f values can be obtained if the die temperature is reduced to 350 °C during squeeze-casting. However, this also increases the risk of premature freezing of the melt in the die cavity during squeezing. Hence, investigation of an optimum combination of squeeze-casting variables can be the subject of a new, separate study.

Although squeeze-casting produced the highest σ_{ULT} and ε_f values, it is found in Table III that SDAS of a squeeze-cast microstructure is greater than that found in a casting made into the same mild steel die at 350° C. Thus, elimination of interdendritic microporosity is more important than the reduction of SDAS. Another advantage of squeeze-casting is that it does not necessitate alloying additions to increase the strength, as is done in commercial Zn–27% Al castings. In a recent study, Zn–8% Al and Zn–27% Al alloys have also been reinforced by fibres of alumina, carbon or steel using only the squeeze-casting technique [10].

3.3.2. Hardness variation in cylindrical castings

For hardness measurements all cylindrical castings were sectioned along their longitudinal axes into two halves as seen in Fig. 1. The sectioned inside and outside surfaces of each sample were polished before taking Vickers hardness (VH) measurements along the height of both surfaces. Table V illustrates the VH variation at 4.0 mm (0.16 in.) intervals from top to bottom ends of each polished surface in those 1.00 in. (25.4 mm) high cylinders cast with 100 °C melt superheat.

In a pure Zn–27% Al alloy the outside surface is significantly harder than the sectioned surface of the casting. On both surfaces the largest hardness values are approached near the top regions, then they decrease gradually and attain their smallest values near the bottom face of the casting. The hardness variation is a result of distribution of the harder aluminium-rich dendrites and also interdendritic microporosity in the microstructure. Since solidification starts at the mould walls, the outside surface contains more aluminium-rich dendrites than the centre of the casting. In addition, due to their smaller density the free aluminium-rich dendrites rise to the melt surface during freezing of the casting. As a result, the largest hardness (90.8 VH) is found on the top of the outside surface, whereas the bottom centre of this sectioned surface has only 39.9 VH. This hardness variation follows closely the chemical analysis in Barnhurst *et al.* [4] who found that in Zn–27% Al alloys the aluminium content increases from bottom to the top of the castings.

In Table V it is seen that the average hardness increases, whereas hardness variation decreases, following strontium and lithium additions. There still exists a difference between the hardness values of outside and sectioned surfaces; however, the hardness changes relatively little along the height of each surface. The largest average hardness (119.5 VH) is reached on the outside surface of the Zn–27% Al alloy containing 0.1% Li. It appears that the hardness variation is reduced when the underside shrinkage problem is reduced. Having an appreciable solid solubility in aluminium, lithium hardens all aluminium-rich phases in the microstructure. As a result, lithium is more effective in increasing the average hardness and reducing the hardness variation in castings.

4. Conclusions

1. The underside shrinkage problem should be overcome without degrading the mechanical properties.
2. Both strontium and lithium reduce the underside shrinkage problem and increase cast quality. Lithium, however, also improves the mechanical properties.
3. Squeeze-casting can be not only a solution for the underside shrinkage problem but also sharply increases the mechanical properties.

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