THE EFFECT OF TRACE LEVELS OF NI AND V ON THE MICROSTRUCTURE AND PROPERTIES OF FOUR COMMON ALUMINUM ALLOYS

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Abstract

The effect of nickel and vanadium with concentrations from <100ppm to ~550ppm on microstructure, mechanical properties and corrosion behavior has been investigated for aluminium alloys 356, 6060/6063, 3004 and 5182. While the Ni and V additions appeared to have no adverse effect on strength, ductility was reduced by the presence of Ni but it was improved by the presence of V for all alloys. Low Ni combined with high V levels gave the best corrosion performance in all four alloy systems. However, there was no difference in corrosion between alloys with low (50ppm) Ni and low (150ppm) V and other combinations. It appears that Ni and V levels may be allowed to increase together within current alloy specifications without detrimental effects on properties. However, high Ni and low V concentrations may reduce ductility and corrosion performance. Some caution should be exercised in allowing Ni to increase alone.

Introduction

Aluminum smelters and anode coke suppliers are formulating strategies to tackle increasing metal impurity (nickel and vanadium) concentrations arising from changes in petroleum coke (PET coke) quality. As smelter demand out strips the supply of low V/Ni green coke sources, the average levels of these metal impurities in anodes and in smelter metal is creeping up [1-6]. There is a lack of property data regarding the effect of Ni and V particularly at low levels as reviewed in [6]. Recently we published initial results in A356 and 6060 alloy [7]. Others have also begun to characterize the effects of Ni and V [8-11]. This paper presents further results in A356 and 6060 and also 3004 and 5182.

Investigation

Compositions tested were based on desire to see any effects of changes in properties within the current alloy specifications. The previously reported work tested 356 and 6060 at low levels (<50ppm Ni, ~100ppm V) and medium levels (~300ppm of Ni and V both). These compositions were nominally repeated in the study reported here. We use the following nomenclature in the paper to identify the alloy compositions; a two letter code "alloy-Ni level, V level", where a high level of the impurity addition is identified as "H", a mid-level as "M" and a low level as "L". For example the alloy A356 with high Ni and low V is referred to as A356-HL. The target low levels are less than 150ppm (typical smelter product), the mid-levels around 250-300ppm (near the max of the P1020 specification) and the high levels around 550ppm (near the 0.05% others max specification on these alloys). Samples were analyzed by optical emission spectroscopy of the original melts. Compositions are given in wt%, except Ni and V analyses in ppm (Tables 1&2).

A356 samples were cast into an improved low pressure sand mould, given a T6 treatment and naturally aged for 24 hrs at room temperature and then aged at 160 °C for 4 hrs. Alloy 6060 (also meeting the 6063 spec) was cast in 50mm slugs for extrusion

using a steel mold, homogenised at 575-580°C for 2.5 hrs, followed by a forced air cool. Material was extruded or rolled, followed by solution treatment at 575 °C for 2.5 hrs, natural ageing for 24 hrs at room temperature and further ageing at 190 °C for 6 hrs. Extrusion slugs 22 mm long and 28 mm Ø were extruded using a laboratory-scale extrusion press to form bars of 5.4 mm Ø. The extrusion temperature was 450°C and the ram speed was 15 mm/s. The peak extrusion load was measured and there was little effect measured although it is possible that increased V levels may increase the extrusion load very slightly.

6063, 3004 and 5182 were cast as plates on a copper chill mold and heat treated and rolled. 3004 was homogenised at 610 ±10ºC for 4hrs followed by a forced air cool. The 16mm thick as-cast samples were milled to 11mm to remove the cast surface. The material was preheated to 450°C and held for 30 minutes. An initial roll pass reduced the thickness to 5.2mm before returning to the furnace for 10 minutes at 450°C and a second roll pass further reduced the thickness down to 2.4mm. After rolling the samples were allowed to air cool.

Table 1: Chemical analyses of 356 and 6060/6063 test alloys.

Alloy ID	Ni (ppm)	V (ppm)	Si	Fe	Mn	Mg	Ti
Spec.	Others each 0.05 wt% Others total 0.15 wt%		6.5-7.5	0.20	0.05	0.30-0.40	0.20
A356-LL	44	155	6.98	0.16	0.05	0.38	0.10
A356-HL	590	150	6.96	0.16	0.05	0.37	0.10
A356-LH	50	580	6.92	0.17	0.05	0.38	0.10
A356-MM	220	220	6.93	0.17	0.05	0.37	0.11
A356-HH	580	560	6.91	0.17	0.05	0.37	0.09
6060 spec.	Others each 0.05 wt% Others total 0.15 wt%		0.30-0.6	0.10-0.30	0.10	0.35-0.6	
6063 spec.			0.20-0.6	0.35	0.10	0.45-0.9	0.10
6063-LL	50	145	0.45	0.21	0.04	0.46	0.01
6063-HL	470	120	0.47	0.20	0.04	0.46	0.01
6063-LH	60	510	0.49	0.21	0.04	0.48	0.01
6063-MM	190	160	0.47	0.20	0.04	0.46	0.01
6063-HH	500	500	0.48	0.21	0.04	0.48	0.01

Table 2: Chemical analyses of AA3004 and AA5182 test alloys.

Alloy ID	Si	Fe	Cu	Mn	Mg	Ni (ppm)	V (ppm)	Ti
3004 Spec.	0.30	0.7	0.25	1.0-1.5	0.8-1.3	Others each 0.05 wt% Others total 0.15 wt%		-
3004-LL	0.22	0.48	0.12	1.14	1.11	60	190	0.01
3004-HH	0.22	0.48	0.12	1.12	1.11	570	480	0.01
3004-LH	0.21	0.38	0.12	1.29	1.13	60	520	0.01
3004-HL	0.22	0.39	0.12	1.27	1.12	560	160	0.01
5182 Spec	0.20	0.35	0.15	0.20-0.50	4.0-5.0	Others each 0.05 wt% Others total 0.15 wt%		0.10
5182_LL	0.14	0.24	0.07	0.39	4.33	50	160	0.01
5182_HH	0.14	0.24	0.07	0.39	4.42	580	440	0.01
5182_LH	0.13	0.22	0.07	0.40	4.42	50	460	0.01
5182_HL	0.12	0.23	0.08	0.41	4.51	600	140	0.01

Tensile testing was carried out at a strain rate of 0.003/s (crosshead speed 5 mm/min). The specimens were ASTM sub-size, 6 mm width, 3 mm thick and 25 mm gauge length. Microstructures were characterized by optical microscopy and scanning electron microscopy (SEM). Phases were identified by energy dispersive x-ray spectroscopy (EDX). Some Vickers hardness tests were carried out to complement the tensile testing work. Salt spray and linear polarization resistance corrosion testing was done. Methodology is further detailed in our previous paper [9].

Results

Microstructure

For all alloys there was no discernable effect of Ni and V on grain size or in A356 any significant change in the dendrite arm spacing. The grain size in the post-extruded condition for the 6060/6063 alloy was approximately 50 µm for all Ni and V combinations. For A356. the secondary dendrite arm spacing (SDAS) was around 45 µm at low levels of Ni and V and it decreased with increasing Ni and V(Figure 5).

In the previous investigation [7], the Ni in the as-cast A356 with 0.029% Ni and 0.03% V was found to be mainly present in the π-phase. In addition there were a small number of very small particles with very high Ni, moderate Si, minor amounts of Mg (~1wt%) and no detectable Fe (labelled as AlSiNi, but with unknown stoichiometry) (Figure 1). Previous findings of the heat treated microstructure (T6) showed that Ni levels above 0.02% Ni led to the formation of a new phase containing Al, Si, Fe and Ni, probably α-AlFeSi with bcc structure. The Ni concentration was highest in the cubic α-AlFeSi phase, followed by the π-$Al_8FeMg_3Si_6$ phase, and lowest in the β-Al_5FeSi phase. This study appeared to support the previous findings.

This finding is also consistent with other work on A356 samples with varying Ni levels (and no added V) [3], where it was found that in a 0.02% Ni containing sample, π-$Al_8FeMg_3Si_6$ phase was the predominant intermetallic phase, with a higher Ni concentration than that in the 0.008% Ni sample. In addition, a very small amount of β-Al_5FeSi phase was observed and the Ni concentration was higher in the β-Al_5FeSi phase than in the π-

$Al_8FeMg_3Si_6$ phase. In a 0.05% Ni containing sample, apart from the π-$Al_8FeMg_3Si_6$, an additional phase with surprisingly high Ni concentration was present.

V does not appear to partition into the intermetallic phase when it is present without Ni, indicating that V tends to reside in the Al matrix as solute. However, when 0.06% V is present with 0.06% Ni, there is some partitioning of V into the α-AlFeSi phase (Figure 2).
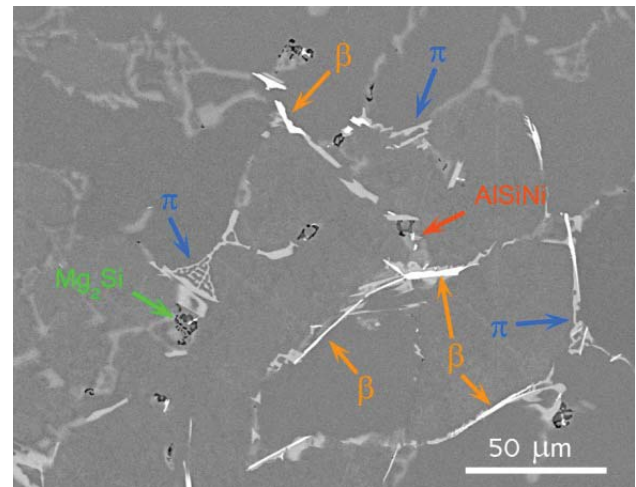

Figure 1 Backscattered SEM image from previous study [7] showing typical forms of all minor phases in as-cast A356. Image taken near chill surface.

In the extruded 6060 alloy (Figure 3), the intermetallic phases were identified to be either hexagonal α-AlFeSi or body-centred cubic α-AlFeSi. V seems to have no effect on the intermetallic phases even with the presence of Ni. Ni tends to partition into the intermetallic phases, especially the body-centred cubic α-AlFeSi. Higher levels of Ni were measured in the intermetallic phases for the Ni+V added alloys compared to the standard alloys. V probably resides in the Al matrix as solute. No increased V levels were detected in the intermetallic phases for the Ni+V added alloy.
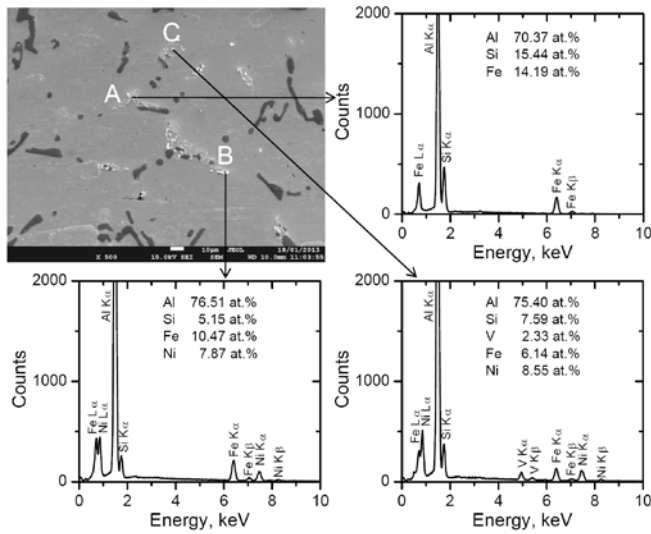
Figure 2. Identification of intermetallic phases by EDX in the A356-0.06V-0.06Ni sample. The predominant intermetallic phase is still β-Al₅FeSi (A), with no or a little partitioning of Ni. A possible bcc α-AlFeSi phase is formed, without (B) or with (C) V partitioning.

Figure 3 Identification of intermetallic phases by EDX in the AA6060-0.05Ni (HL) sample. The intermetallic phases are probably either bcc a-AlFeSi (A) or hexagonal a-AlFeSi (B), with the former containing significantly higher Ni than the latter.

For rolled AA3004, there appears no influence on intermetallic phases with a level of 0.05% V. Two major intermetallic phases are present: one containing Al, Fe and Mn while the other containing Al, Si, Fe and Mn. These phases are probably $Al_6(Fe,Mn)$ (A) and α-$Al_{12}(Fe,Mn)_3Si$ (B). Ni levels above 0.02% results in the formation of a new intermetallic phase containing mainly Al, Fe and Ni, probably Al_9FeNi, although there is no partitioning of Ni into the $Al_6(Fe,Mn)$ (A) and α-$Al_{12}(Fe,Mn)_3Si$ (B) phases (Figure 4).

For rolled AA5182, 0.05% V appears to have no influence on intermetallic phases. Ni levels above 0.02% lead to the formation of a new intermetallic phase containing Al, Mn, Fe, Ni and Cu (Figure 5). The crystal structure of this new phase remains unknown.

Mechanical Properties

Given the scatter in strength measurements, it is difficult to discern trends in the strength property variation for the different levels of Ni and V in A356 alloy, however, high V levels seem to improve the ductility and high Ni levels seem to decrease ductility (Figure 6).

There seems to some effect on mechanical properties in 6063 with different Ni and V levels but the exact trends are hard to discern (Figure 7). For example the HL sample has a much lower ductility than the base alloy or those with higher V levels (MM & HH). However, the UTS and 0.2% yield stress show no consistent trend. As with the observations in A356, it may be that Ni has a detrimental effect on ductility but this is offset by V addition which improves ductility.
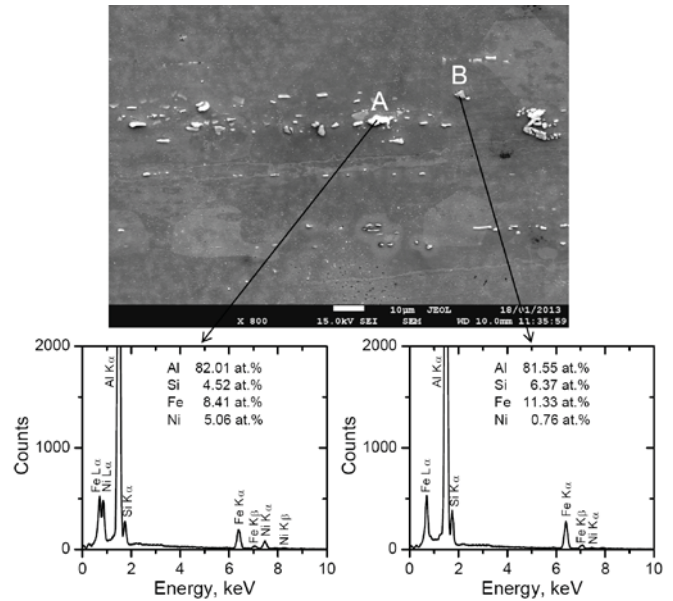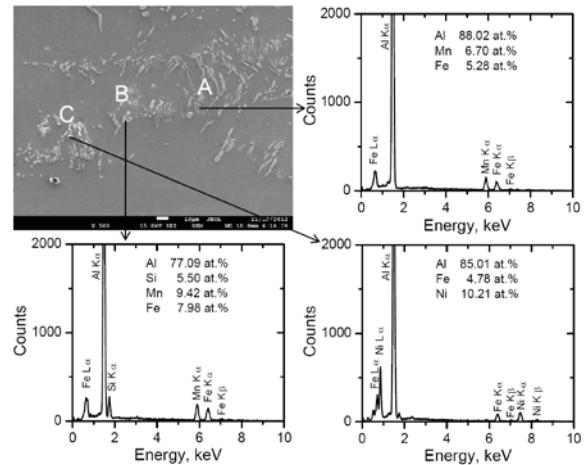

Figure 4 Identification of intermetallic phases by EDX in the AA3004-0.05Ni (HL) sample. There is no partitioning of Ni into the $Al_6(Fe,Mn)$ (A) and a-$Al_{12}(Fe,Mn)_3Si$ (B) phases. The level of 0.05% Ni leads to the formation of a new phase (C) containing mainly Al, Fe and Ni, which is probably Al_9FeNi.
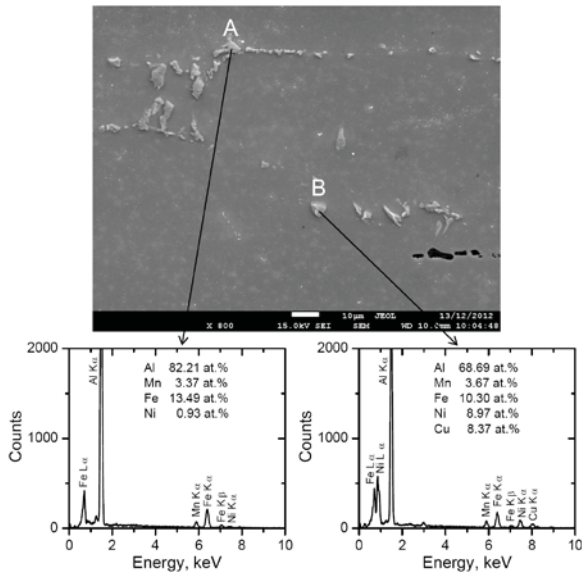
Figure 5 Identification of intermetallic phases by EDX in the AA5182-0.05Ni (HL) sample. There is slight partitioning of Ni into the Al6(Fe,Mn) phase (A). The level of 0.05% leads to the formation of a new phase (B) containing Al, Mn, Fe, Ni and Cu.

As with the other alloys, there is no clear trend in strength variation with Ni and V addition for 3004. However, there is a drop in ductility with high Ni addition (Figure 8). Varying Ni and V levels do not appear to have a consistent effect on alloy 5182 (Figure 9). Whilst the lowest ductility is found when the Ni and V contents are highest, neither the Ni addition or the V addition appeared to reduce the strength.
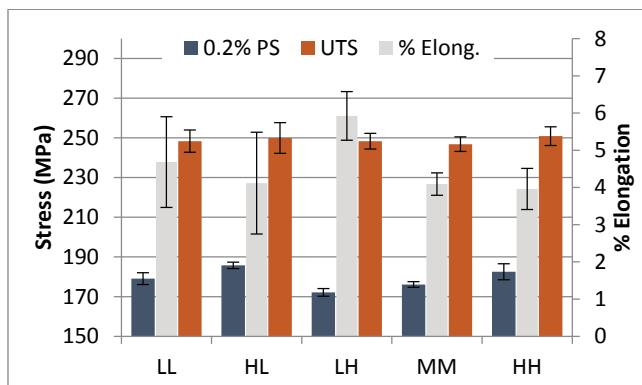
Figure 6 Mechanical properties of 356 with varying Ni and V levels.

Corrosion

The only consistent trend in corrosion performance across the alloys is that the LH alloy in each case has the lowest current density (Figure 10), implying that low nickel and higher vanadium concentration improves corrosion performance. The salt spray tests showed greater variation on the surface of each sample than from sample to sample variation for a given treatment of different Ni and V concentrations, although there was some evidence that particularly in the 3004 alloy that the higher Ni content alloys showed greater corrosion than the other alloys.

It should be noted that the tested specimens were covered by residual of die spray materials and oxide from the heating process. Such surface conditions might have a significant influence on the corrosion performance. We plan to remove these surface layers and examine the corrosion resistance in future work, including polarization, salt spray, surface observation and mass loss.
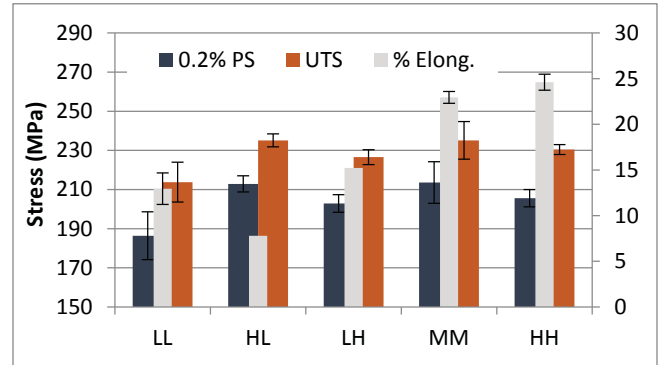

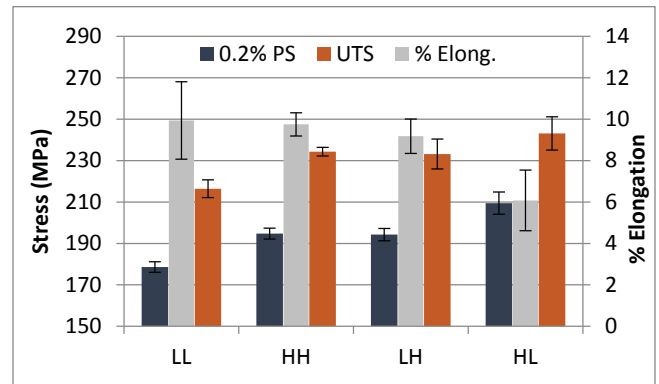*Figure 7 Mechanical properties of 6060 with varying Ni and V levels.*

Figure 8 Mechanical properties of 3004 with varying Ni and V levels.
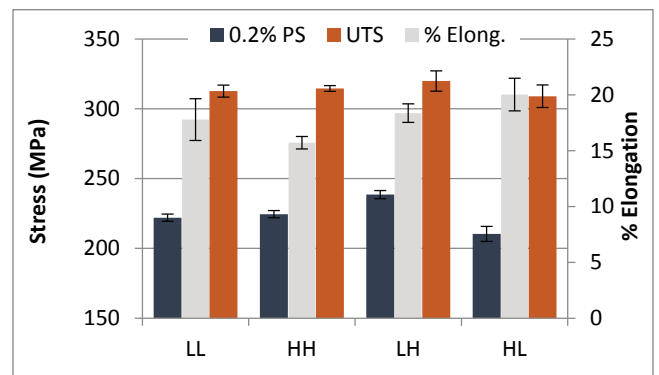

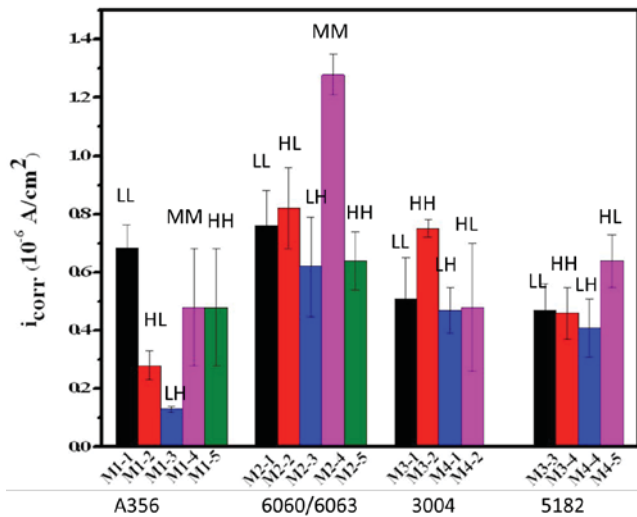*Figure 9 Mechanical properties of 5182 with varying Ni and V levels.*

Figure 10 Corrosion current density for all alloys tested.

The potentiodynamic polarization curves do show that which increasing Ni and V content that the current density on the anodic side of the curve is increased whilst the cathodic side is decreased, although the size of the effect varies considerably between the alloys (Figure 11) indicating that increasing corrosion rates are due to anodic activation in the samples.

Discussion

It is clear that Ni at increased contents partitions into the Fe containing phases. There is also some evidence that it does not partition equally into the different phases. V has little effect on the Fe-containing intermetallics and appears to be present in the matrix. This is not surprising as Ni shows very strong segregation into intermetallics with a partition coefficient even lower than for Fe in Al alloys. Al-V, however, is a weak peritectic which means that it partitions slightly into the α-Al phase during solidification.

In general, there was little effect from the different levels of Ni and V however two effects which were observed were;
i)   Ductility (elongation) seems to be reduced by the presence of Ni and improved by the presence of V although the effect seems clearer in some alloys, e.g. A356 than others, e.g. 5182.
ii)   Low nickel and high vanadium addition (LH designation) gives the best corrosion performance in all four alloy systems. However, the difference between alloys with low Ni and Low V (LL) and other combinations (MM, HL, HH) was subtle.

The effect on ductility is typical of systems with an increase in brittle intermetallics. An increase in the amount of intermetallic, particularly acicular ones, leads to easier crack propagation. There is little increase in strength due to their size and morphology asthey are not effective barriers to dislocation motion.
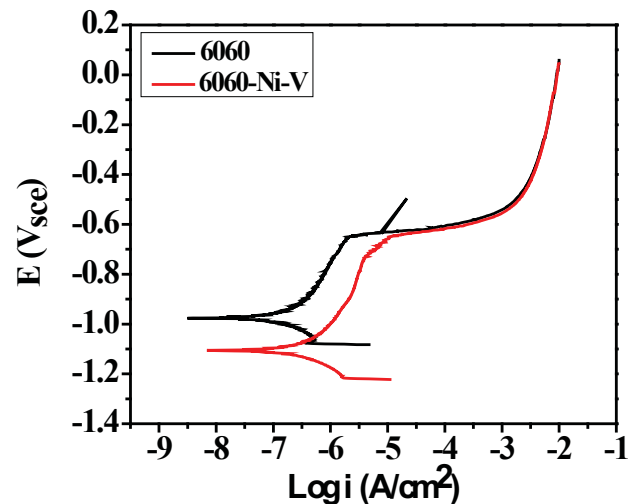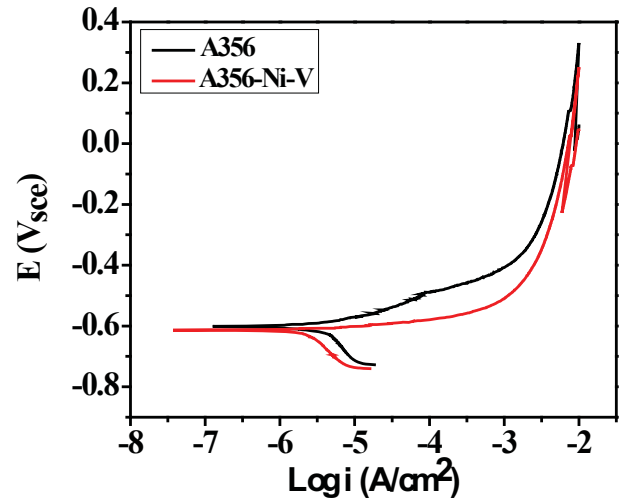

Figure 11 Polarisation curves of A356/A356-LL & MM and 6060/6060 LL-MM.

The corrosion results indicate that low nickel and high vanadium improves performance. This could again be due to nickel increasing the amounts of cathodic iron containing intermetallics and or the nickel present in these intermetallics can increase their potential compared to the matrix increasing the driving force for corrosion. Vanadium on the other hand in the matrix seems to increase the potential of the matrix and decrease the potential difference in the micro-galvanic cell. This is often an effect of elements soluble in the matrix. However, the potentiodynamic polarization plots indicate that any increase in corrosion appears to be due to anodic activiation, so it may be that the increased corrosion rate is more closely related to the degretation of any protective oxide film as much as changes in the microgalvanic potential difference. The effect of Ni and V on corrosion of these alloys clearly requires more careful study.

Conclusions

In general, it appears that Ni and V levels can be increased together within current alloy specifications with little detrimental effect. However, if *high Ni low V* coke were to be used, which would result in high Ni and low V concentrations in Al alloys, the ductility may reduce. Further testing is needed to confirm this. The potential beneficial effect of V on corrosion performance needs further investigation.

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