

EFFECT OF VANADIUM ADDITIONS ON THE STRUCTURE OF ALUMINIUM (AL99.5) AND 6XXX ALUMINIUM ALLOYS

S.Boczek¹, M.Lech-Grega¹, J.Morgiel², K. Piela³

¹Institute of Non-Ferrous Metals Light Metals Division; 19 Pilsudskiego Street, Skawina 32-050, Poland

²Institute of Metallurgy and Materials Science, Polish Academy of Sciences; 25 W.Reymonta Street, Kraków 30-059, Poland

³AGH University of Science and Technology; 30 A.Mickiewicza Av., 30-059 Krakow, Poland

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Abstract

Vanadium additions of up to 0.4% introduced to the 6xxx series aluminium alloys affect their plastic properties. The mechanism of vanadium effect on the aluminium alloy structure is not fully understood.

The influence of vanadium additions on the precipitation of Mg₂Si and Al₂Cu phases in various stages of the technological process was investigated.

To explain the phenomenon of microstructural changes, TEM examinations were performed on a high-purity aluminium (Al99.5) with 0.2% V after casting and heat treatment.

After ageing, higher vanadium content in the 6xxx series aluminium alloys reduced the degree of strengthening with Mg₂Si and Al₂Cu phases and increased the content of AlFeSi and AlMgV particles in the range of sizes from 50 to 500nm. The high-resolution observations indicated that after 4 hours of aging, in the 6xxx series alloys, coherent strengthening phases were formed.

It was found that in aluminium alloys during plastic working, AlV particles may act as inhibitors for the newly created AlFeSi and AlMgV phases.

Introduction

Vanadium in cast and wrought aluminium alloys starts in recent years playing a significant role.

On the one hand, due to the new sources where starting materials are acquired for the production of anodes in a process of electrolysis, the role of vanadium addition is not always positive, because of some changes that it introduces to the properties of cast and wrought aluminium alloys [1].

On the other hand, it is the fact well-known that aluminium alloys with the addition of vanadium have been used in recent times for the structural components of vehicles.

There are indications that aluminium alloys containing vanadium are characterised by an ability to absorb kinetic energy, particularly important feature of the material, taken into consideration when assessing the properties of vehicle components subjected to strong deformation in the crumple zone in case of accidents (low ratio of R_{p0.2}/R_m and large reduction of area Z).

Industrial research carried out on the 6xxx series aluminium alloys containing up to 0.2 wt% vanadium focussed largely on testing of the mechanical properties. Particular interest enjoys alloy 6069 as compared to 6061. Higher properties such as R_m and R_{p0.2} have been reported for alloy 6069 in the T6

condition, which is undoubtedly associated with a higher content of the strengthening elements like Mg and Cu. The effect of vanadium content on the 6069 alloy has not been examined [2-5].

It is believed that the introduction of vanadium causes grain refinement, reduces the conductivity and increases the temperature of recrystallisation. While investigating the 6063 alloy with 0.1wt% addition of vanadium, it was found that the presence of vanadium accelerated the precipitation kinetics of magnesium-silicon β' and β" phases, which in turn had an impact on the tensile strength and yield strength of the material in the T6 condition [6]. In AA6063 alloys containing 0.038 wt% of vanadium, the presence of this element in the intermetallic compounds of α AlFeSi is not known to occur [1].

In AlMgSi alloys after precipitation hardening, the addition of 0.15wt% vanadium reduced the size of the grains and the yield strength, while increasing the tensile strength by about 10% [7].

From the Al-V phase equilibrium diagram it follows that the solubility of vanadium in aluminium (in the solid state) is 0.37 wt% at a temperature of approximately 660°C, and up to the vanadium content of about 9wt%, the Al₂₁V₂ phase occurs [8]. So, one would expect in aluminium alloys containing vanadium in an amount of 0.25wt%, especially after heat treatment, the presence of fine phases containing this element.

In studies of the 6xxx series alloys containing copper it was found that the addition of 0.2 wt% vanadium increased the elongation in the tested alloys. After aging for 4 hours, a change was observed in the morphology of the Mg₂Si phases in the material without the addition of vanadium as compared to the material containing 0.2wt% of this element. It was also found that in vanadium-containing alloys, the dispersoids of Mg₂Si were larger and less spread in the aluminium matrix. The addition of vanadium increased the quantitative share of small precipitates, and contributed to a change in their shape [9].

The available data do not explain, however, what role vanadium can play in the microstructure of 6xxx series alloys. Therefore, the aim of this study was to analyse the effect of vanadium additions in an amount of up to 0.2wt% to the commercial 6xxx series alloys containing also copper on the precipitation of fine phases in a matrix after the successive stages of technological process.

Methodology

The test material was composed of samples cast from the high-purity technical grade of aluminium containing 0.2 wt% of vanadium - AV02 samples, and from samples extruded from

the 6xxx series aluminium alloys containing vanadium in the following amounts: 0wt% - V0 samples, 0.2wt% - V02 samples, 0.1 wt% vanadium and 0.7 wt% copper - RV01 samples, and 0.2wt% vanadium and 0.7 wt% copper - RV02 samples. From the 6xxx alloy, ingots were cast by semi-continuous method (DC Direct Cast) with a diameter of 100 mm. They were next homogenised and extruded into circular rods with a diameter of 20mm. The extruded rods were subjected to a heat treatment carried out in the following regime: solutioning at 530°C/2h and aging at 175°C/4 hours to give the T6 condition.

Thin films were prepared by grinding and electropolishing. The structure of the precipitates occurring in the alloys was examined on the transmission electron microscopes - HR-TEM Tecnai G² with FEG and (S) TEM Tecnai G² 20 200kV with HAADF (high-angle annular dark field) detector and an attachment to identify the chemical composition by EDS (Energy Dispersive Spectroscopy). Quantitative analysis of the precipitates in a range of 50 to 800nm was performed on the images obtained from a SEM Inspect F50 scanning electron microscope, taking 4 images for each of the samples.

Results

TEM observations had as a main aim structure analysis of the vanadium-containing alloy in successive stages of the manufacturing process. Depending on the amount of the alloying

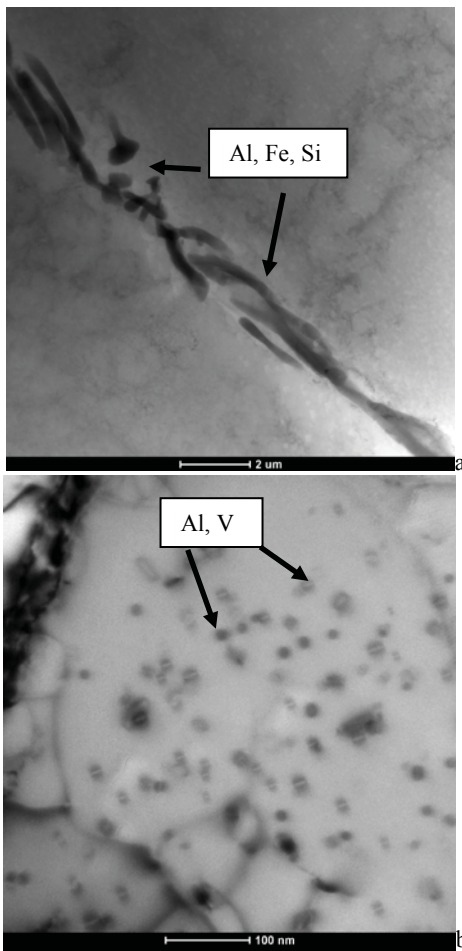


Fig.1 Microstructure of the as-cast AV02 sample: a) precipitates on the grain boundaries, b) fine precipitates inside the grains

elements such as vanadium and copper, their different effect on the image of the microstructure and on the morphology of the resulting precipitates was observed. For comparison, the 99.5 aluminium alloy with 0.2wt% vanadium (AV02) was also cast to characterise the vanadium behaviour in the alloy structure.

The microstructure of the cast AV02 alloy was observed to contain coarse phases with Al, Fe and Si (Fig. 1a) present on the grain boundaries and very fine phases (about 10 nm) with elements such as Al and V occurring inside the grains (Fig. 1b). The ALV phases occurred in clusters inside the grains and were spread throughout the whole area of the sample examined.

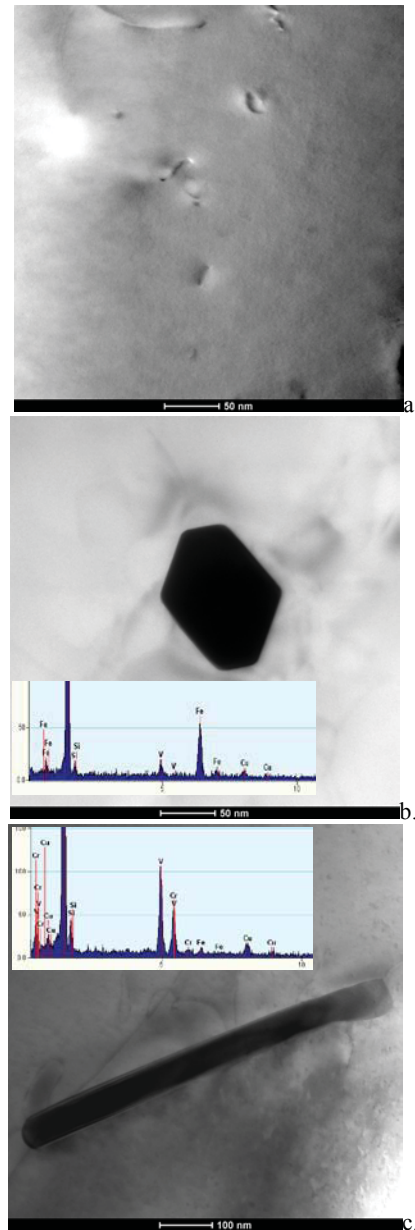


Fig. 2 Structure and chemical point analysis of the sample a) V0, b) V02 c) RV02 after solutioning

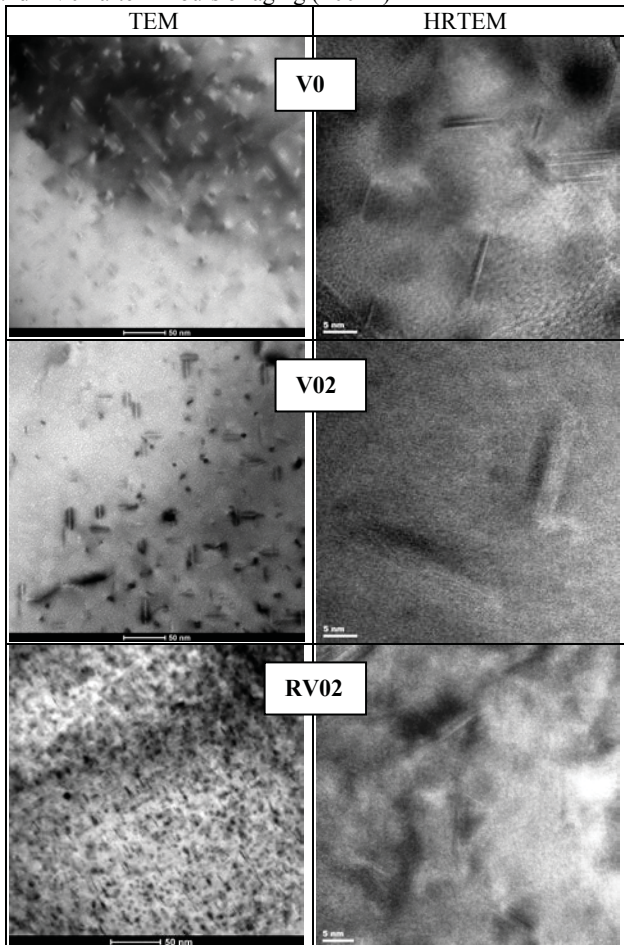
In the RV01 sample after extrusion, two types of the precipitates were observed, i.e. of rhombohedral shape and of rod-like shape in the range of sizes from 50 nm to 700 nm. The

presence of large precipitates of the size above 1 μm , characterised by oblong and circular shapes, was also reported.

The structure of samples after solutioning was free from any traces of the fine-dispersed strengthening phase. There were also no traces of the coarse phases along the grain boundaries that would confirm the low cooling rate after the solutioning heat treatment (Fig. 2). On the other hand, in sample without the addition of vanadium (V0), large precipitates (above 500nm) were present, which mainly included elements such as Al, Fe, Si, and occasionally Mg, Ni and Cr. In samples that contained vanadium (V02) and vanadium and copper (RV02), fine precipitates (in the range of 50nm to 500nm) were noted to be present. Their chemical composition was dependent on their shape (Fig.2b, c). Rod-like shaped precipitates were composed of the phases of two types: AlVMg with the angular rod ends and AlFeVSi. The AlFeVSi phases in the RV02 samples additionally contained Cu. The rhombohedral and oval precipitates were of complex character, based on elements such as Al, Fe, Si. The interchangeable elements, whose presence was not always traced during the analysis, were elements such as Mg, V, Cu, Cr, Ni, Mn (Fig.2).

The microstructure of samples V0, V02 and RV02 after 4 hours of aging was found to have three types of phases: finely-dispersed strengthening phases, fine phases of the size from 50 to 500 nm, and iron phases of the size $> 500 \mu\text{m}$.

Table I The microstructure of samples and high-resolution images of the strengthening Mg_2Si and Al_2Cu phases in samples V0, V02 and RV02 after 4 hours of aging ($<001>$)



Strengthening phases of Mg_2Si and CuAl_2

In samples V0 and V02, the strengthening phase was Mg_2Si phase. In sample RV02, two strengthening phases, i.e. Mg_2Si and CuAl_2 , were present. It was also observed that the size and the distance between the finely dispersed Mg_2Si precipitates was different in the examined samples. The precipitates of Mg_2Si in sample V02 were larger and spacing between the dispersoids was also larger compared to the sample without vanadium (V0) (Tables I). Quite different appearance had the images of sample RV02, where the alloy was additionally strengthened by the CuAl_2 phase. Larger amount of dispersoids was observed there, compared to the V0 and V02 samples (Table I).

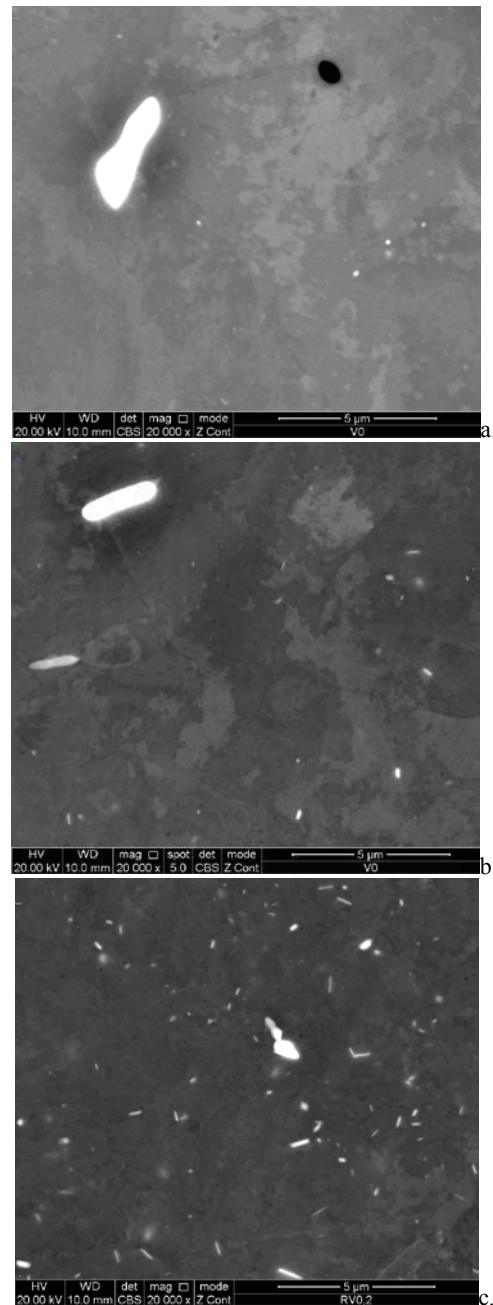


Fig. 3. Microstructure of samples a) V0 - 34 precipitates/ 1mm^2 , b) V02 - 231 precipitates/ 1mm^2 , and c) RV02 - 579 precipitates/ 1mm^2 as observed by HR-SEM.

Based on the high-resolution observations carried out under a HR-TEM Tecnai G² with FEG, the relationships obtained previously were confirmed, and it was found that the strengthening Mg₂Si phase is semi-coherent with the matrix in all the three samples examined.

Fine phases of the size from 50 to 500nm

The chemical composition of fine precipitates with sizes ranging from 50 to 500nm, present in samples V02 and RV02 after aging, has not changed compared to the same samples examined after solutioning. There was only slight increase in the size and shape of the precipitates after 4 hours of aging. The RV02 sample had the greatest quantity of fine phases compared to the V0 and V02 samples. In sample V0, the precipitates of this size occurred only sporadically, as in the same sample after solutioning.

To confirm the quantitative results obtained by TEM, studies were conducted on HR-SEM to analyse larger sample areas, and hence to take measurements on a larger number of the precipitates (Fig. 3).

The performed statistical analysis shows that in the V0 sample, 34 precipitates fall to 1mm², while in the V02 sample there are 231 precipitates, and in the RV02 sample – 579 precipitates. The quantitative share of the precipitates, compared for samples without vanadium (V0) and with vanadium (V02), has increased six times, and two times when a comparison is made between samples V02 and RV02.

Iron phases of the size > 500 μm

The morphology and chemical composition of iron phases in individual alloys did not change after the processes of extrusion, solutioning and aging. Coarse phases of AlFeSi also contained Mn, Ni, Cr and Cu in alloy RV02. These phases did not contain vanadium.

Conclusions

In the cast AV02 sample, the presence of small precipitates of AlV located in clusters inside the grains was revealed. Additionally, the aluminium matrix also contained small amounts of vanadium.

In the 6xxx series alloys after extrusion, the addition of vanadium caused the occurrence of a large amount of the fine precipitates of a size from 50 to 500nm. This increase could be related with:

- the occurrence of minor phases containing Al and V after the casting process, which might act as nuclei for the formation of such phases as AlFeSiV and AlVMg,
- reduced stacking fault energy, which leads to the generation of higher dislocation density as a result of the additions of vanadium and copper dissolved in matrix during the extrusion process.

After the aging process (175°C/4h), changes were observed in the morphology of Mg₂Si phases in samples V0 and V02. It was found that in samples containing vanadium, the dispersoids of Mg₂Si were larger and less spread in the aluminium matrix. The reason for this could be the depletion of the solution in elements such as Mg and Si, due to the precipitates of AlFeSiV and AlVMg arising in the process of plastic forming. In samples containing vanadium and copper (RV02), the second CuAl₂ phase strengthening the alloy occurred. It filled the spaces between the dispersoids of the Mg₂Si phase.

Vanadium and copper additions in the alloy not only caused a significant increase in the quantity of fine precipitates in the range of 50 - 500nm, but also influenced the formation of precipitates of various shapes and chemical composition. It was found that in the RV02 alloy there were two types of precipitates in the shape of rods containing Al, Fe, Si, Mg + V and/or Cu as well as Al, Mg and V. The second group present in the RV02 alloy consisted of rhombohedral precipitates whose chemical composition was a combination of Al, Fe and Si together with Mg, V, Cr and Cu.

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