

Electrodeposition and characterisation of Al-W alloy films from ionic liquid

D Hühlich, D Wachner, M Müller, I Scharf and T Lampke

Institute of Materials Science and Engineering, Chemnitz University of Technology, 09125 Chemnitz, Germany

Abstract. Al-W alloy films were prepared by electrodeposition using anhydrous 1-ethyl-3-methylimidazolium chloride (EMIMCl) ionic-liquid solution with aluminium chloride in a ratio of 1:1.5. As a commercially available tungsten precursor, tungsten hexachloride was used. The metal is dissolved in the ionic liquid at concentrations up to 0.06 mol/l. The deposition took place outside the glove box with a continuous argon stream over the electrolyte at a temperature of 60 °C with a current density of 1 A/m². Resulting alloys show a tungsten content higher than 20 wt% (3.5 at%). The phase composition of Al-W alloys was observed by X-ray diffraction (XRD), and the chemical composition was characterised by scanning electron microscopy (SEM) and inductively-coupled plasma optical emission spectroscopy (ICP-OES).

1. Introduction

Many components can be made from inexpensive and readily available raw materials if they are functionalised by a suitable metallic coating. This should provide protection against corrosion or chemical degradation, impart abrasion resistance, scratch resistance and hardness to the surface, or improve the electrical conductivity. For this purpose, the electrochemical coating of materials out of aqueous electrolytes is used. However, some technically important metals (e.g. aluminium) require deposition potentials where water decomposes electrolytically. As an alternative to aqueous electrolytes, the use of ionic liquids (IL) is possible. ILs are salts with large unsymmetrical ions, which are liquid at a temperature below 100 °C. They possess a high decomposition voltage and thus a larger usable electrochemical window compared to water. As a result, noble metals [1, 2] and very non-noble metals can be deposited from IL without a decomposition of the electrolyte. Further advantages of ILs are the low vapour pressure, low toxicity, and non-flammability. However, the handling of the ionic liquids is complicated due to their strong hygroscopic properties. Even small amounts of water from the surrounding atmosphere can lead to unwanted side reactions such as the release of HCl in chloride-containing ILs. Therefore, working in closed environments (such as a glove box with an inert gas atmosphere) is required. This results in challenges in the production of technically usable metallic coatings. Anhydrous work on an industrial scale is not state of the art due to high costs and the complex technical realisation.

The principles of galvanic deposition from IL are described in the two standard works of H. Ohno [3] and F. Endres et al. [4]. Several reviews have explained the great potential of the IL for the deposition of base metals and semiconductors [5–7]. Among others, aluminium was deposited for example on high-strength steel screws [8]. Aluminium layers are interesting because the metal shows a high resistance to corrosion due the formation of a natural passive film (alumina) on the surface. Therefore, they are suitable as corrosion protection for metals that are more reactive. But these layers can be also damaged



by corrosion. The aluminium is locally corroded by pitting [9]. As an alternative to technically used aluminium alloys, the alloy with tungsten offers good protection against corrosion it by shifting the corrosion potential to a much more positive value [10]. In recent years, attempts have been made to deposit refractory metals from IL. In 2010, Nohira and co-authors deposited tungsten from N-ethyl-N-methylpyrrolidinium chloride (EMPyCl) - ZnCl_2 on Ni at 150 °C [11]. The precursors WCl_4 or WCl_6 were also used in the presence of KF as additive. In the case of WCl_6 precursor, a denser and smoother, but still rough and cracked film was obtained. Al-W alloy films produced by sputtering [12–13], ion implantation [14], laser surface alloying [15], and electrodeposition [16–20] were reported previously. Hirato and co-authors deposited W-Al alloys from IL using a W_6Cl_{12} precursor [21]. In the case of aluminium deposition, the system AlCl_3 -EMIMCl has often been used. In this system, a general problem is the moisture sensitivity of the IL, especially for the chloride-based one. However, the methods listed here have disadvantages for a later technical implementation. The applied thin-film techniques such as sputtering are e.g. not suitable for obtaining layers $> 2 \mu\text{m}$. Processes with specially synthesised precursors such as W_6Cl_{12} are unfavourable for a later scale up. Furthermore, a process that only works in the glove box is difficult to translate into a larger technical framework. Many attempts have been made to use less moisture and air sensitive systems, but until now there is no alternative to AlCl_3 [22]. In consequence, all relevant tests for aluminium deposition are carried out in a glove box under inert gas atmosphere. Initial trials for technical implementation outside a closed facility were carried out for the first time, a steel strip coating succeeded in an open plant [23]. Nevertheless, it is still far from a technical implementation.

The aim of this work is a description of the electrochemical deposition of Al-W layers from ionic liquids outside a glove box with commercially available electrolyte components. In the future, this process can be further developed to a technical application.

2. Materials and Methods

The electrolyte prepared consists of tungsten(VI)-chloride WCl_6 (99,9 %, ABCR) and 1-Ethyl-3-methylimidazolium chloride-aluminium chloride EMIMAlCl₃ ($> 98 \%$, Iolitec) ionic liquid. The molar ratio of EMIM:AlCl₃ was 1:1.5. For the purpose of using the electrolyte outside the glove box, the contact of the electrolyte to water must be avoided completely. All vessels must be thoroughly flushed with argon. Also, all tools must be dry. The substances are highly hygroscopic and/or release HCl on contact with atmospheric moisture. The preparation of 40 ml electrolyte took place in a round bottom flask under argon. Before every experiment, the IL was heated up to 100 °C and dried for 5 h under vacuum at 4 mbar. A Vacuubrand PC 3004 Vario vacuum pump was used. Thereafter, the flask must be put back under the protective Ar atmosphere. Subsequently, the WCl_6 was added, preferably in small portions. It was again dried for 2 days under vacuum (15 mbar) at 80–90 °C until the colour of the electrolyte was clear orange, which indicates the chemical equilibrium. For the galvanostatic deposition, the electrolyte was transferred into an argon-purged vessel, in which a few grams of molecular sieve were submitted. The molecular sieve protects the electrolyte by taking up any traces of water that may be contained in the electrolyte. Figure 1 shows the coating cell for working under non-aqueous conditions.

Steel sheets (5×5 mm) were used as cathode after appropriate pretreatment. As anode, an aluminium sheet with the same size was used. The electrochemical deposition was carried out under constant stirring (100 rpm) with a magnetic stirring bar in the size of 20×5 mm and argon counterflow with a plating temperature of 60 °C. The electrodeposited coating was from a plating bath containing 0.06 mol/l WCl_6 . The Metrom Autolab PGSTAT204 potentiostat was used as power source in the galvanostatic mode. The applied cathodic current density was 1 A/dm² with a deposition time of 3600 s. The potential values were not measured. After the deposition, the cathode was immediately removed from the electrolyte and thoroughly cleaned with ethanol and water. Every deposition was carried out in freshly prepared electrolyte. The deposit morphology and composition was determined with a scanning electron microscope (LEO 1455VP, Zeiss), an X-ray diffractometer with a pointfocus, Lynxeye XE detector and Co-K α radiation (D8 Discover, Bruker AXS) and with the optical emission spectrometry (Optima 8300, Perkin Elmer).

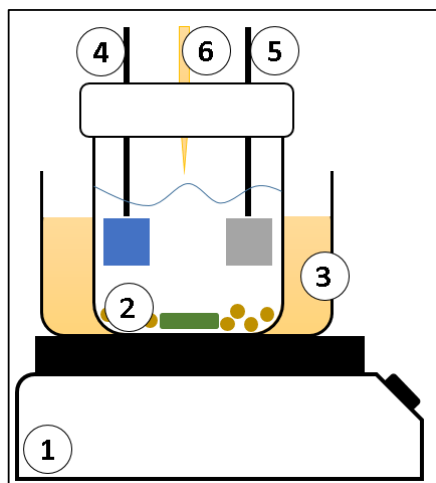


Figure 1. Illustration of the coating cell; with Heater and magnetic stirrer (1), beaker with magnetic stirring bar and molecular sieve (2), oil bath for constant tempering (3), anode (4), cathode (5) and the inert gas inlet (6).

3. Results and discussion

The obtained Al-W deposits were adherent, compact, light to dark grey and evenly dull. The layer thickness is heavily dependent on the flow rate. Too little bath movement (50 rpm) as well as too fast stirring (250 rpm) leads to less layer growth ($< 2\mu\text{m}$). An optimum has been shown at 100 rpm. Likewise, the current density had an influence on the layer properties. Variations between 0.05 A/dm^2 and 1 A/dm^2 showed that a higher tungsten content could be incorporated into the layer with a current density of 1 A/dm^2 . A lower current density lead to a less uniform distribution of the layer thickness. It was also found that for lower current densities the layer thickness distribution became more uneven. The results were increased layer thicknesses in the edge areas with increased tungsten content.

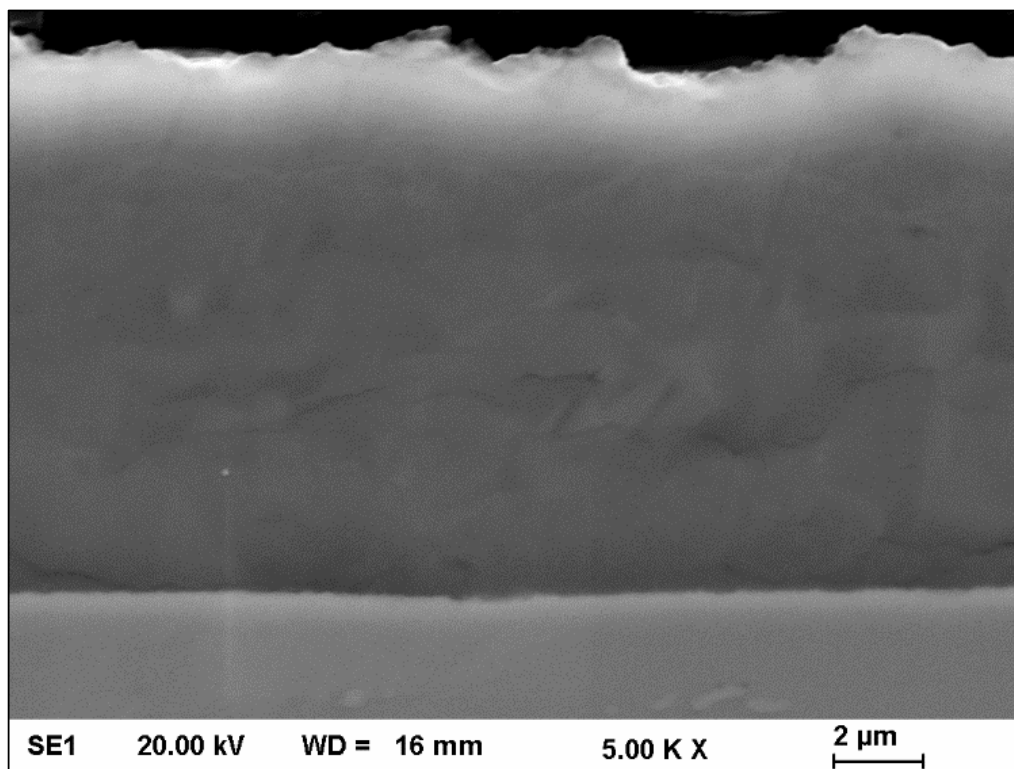


Figure 2. SEM image of the Al-W layer (1 A/dm^2 , $60\text{ }^\circ\text{C}$, 100 rpm, 3600 s) with 20 wt% (3.5 at%) tungsten deposited outside the glove box.

Figure 2 shows the image of the cross-section from the Al–W layer. The resultant layer has a thickness of 16 μm and the tungsten content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) and is 20 wt%, which corresponds to 3.5 at%. For this purpose, an aqua regia digestion was carried out in order to bring substrate and layer into solution. Thus, the measurement was carried out against corresponding standards. Literature shows that the layer becomes more porous with higher tungsten content. Results from the literature show that a firmly adhering layer can contain up to 12.4 at% Tungsten [22]. This shows that the results obtained can be compared with the systems known from the literature and a deposition outside the glove box is possible with commercially available precursors.

Furthermore, X-ray diffraction (XRD) measurements were carried out. A typical diffractogram measured is shown in figure 3. The layer shows a characteristic diffraction pattern for fcc Al. At $2\theta = 45^\circ$ there is a clear peak, which indicates Al {111} and at $2\theta = 52^\circ$ and 77° the peaks of the substrate material Fe. Elemental tungsten was not found because of a clear formation of an Al–W solid solution which was identified due to the shift of the aluminium lattice parameter, which is also in agreement with the literature (figure 4). In addition, the tungsten content is too low and the crystallite size could be in the order of a few nm. Thus, a possible tungsten phase can be X-ray amorphous. Thus, the resulting amorphous phase cannot be measured, which is consistent with the literature findings shown in figure 3 (right). Determined from the peak positions the lattice parameter shows a value of 0.4034 nm, which fits well into the previously known results.

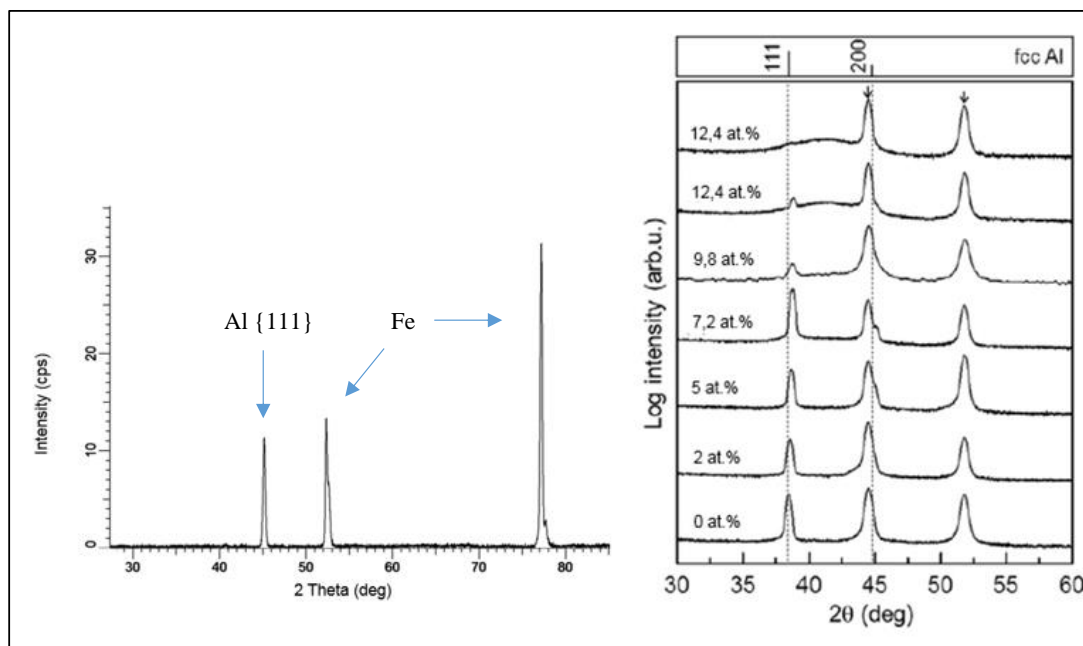


Figure 3. XRD measurement of the Al–W film with 20 wt % (3.5 at%) tungsten deposited outside the glove box (left) and XRD diffraction diagrams of aluminium and Al–W alloy films obtained from EMIMCl–AlCl₃ baths from reference [22] measured with Cu-K α radiation (right).

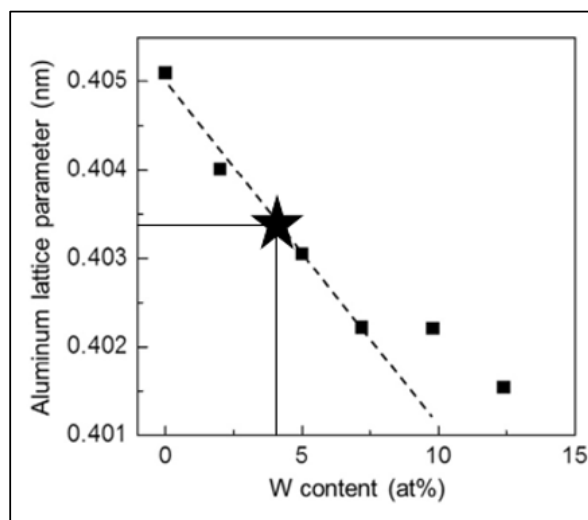


Figure 4. XRD measurement from reference [21], lattice parameter of fcc Al phase in aluminium and Al–W films on Nickel. The star corresponds to the lattice parameter from the measurements in this study.

4. Summary and conclusion

This work shows the successful preparation of Al–W alloys by electrodeposition from an EMIMCl–AlCl₃ electrolytic bath with a concentration of 0.06 mol/l WCl₆ outside the glove box at 60 °C from commercially available substances. The resultant layer has a thickness of 16 µm and a tungsten content of 20 wt% (3.5 at%). Layer studies were carried out using SEM, XRD and ICP-OES. This shows, in good agreement with existing literature, that it is possible to successfully electrodeposite Al–W layers outside closed systems like a glove box and obtain a metallic layer with technically relevant properties.

5. References

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Acknowledgements

The authors acknowledge the financial support by the German “Bundeministerium für Bildung und Forschung” in the joint project “GALACTIF” 13XP5017D. We would also like to acknowledge the VDI Technologiezentrum and all project partners for supporting the research. We would also like to thank Mr Marc Pügner for the XRD measurements and Mr Steffen Clauß for the SEM measurements.