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# MULTISOURCE, MAGNETRON DEPOSITED Al-Cu-Fe THIN FILM COATINGS – THE STRUCTURE AND PROPERTIES

**Keywords**

Magnetron sputtering, thin films, intermetallic phases, Al-Cu-Fe system, tribological properties.

**Abstract**

Thin films of Al-Cu-Fe type have been deposited by means of multisource, DC magnetron sputtering from elemental, metallic targets. The composition of films, studied by the EDS method, has been chosen which is close to the one corresponding to the icosahedral quasicrystalline phase $\psi$-$Al_{62.5}Cu_{25.0}Fe_{12.5}$. X-ray diffraction studies of films deposited at $400^0$C on steel substrates revealed that the cubic $\beta$-Al(Cu,Fe) phase is a dominant one. SEM and TEM techniques have been used for the surface and cross section characterisation of deposits.

Prolonged post annealing of these coatings led to inter-diffusion of components between the steel substrate and the coating. It leads to the change of the phase composition of the coating and the iron-rich monoclinic $\lambda$-$Al_3Fe_{1-x}Cu_x$ phase emerges in the film.

The preliminary studies of microhardness and tribological behaviour show that the film microhardness reaches a local maximum of about 8.5 GPa for the chemical composition close to the one of the quasicrystalline phase. However, the presence of this phase in studied films has not been proven yet. The friction

coefficient values, measured against alumina in ball on disc geometry, oscillate around 0.65 – the value lower than that observed for uncoated 4H13 steel.

## Introduction

The Al-Cu-Fe system is one of numerous multicomponent metallic systems containing phases belonging to the group of quasicrystalline structures, attracting attention of research teams because of their unusual mechanical, electrical and thermal properties [1]. The icosahedral $\psi$-$Al_{62.5}Cu_{25.0}Fe_{12.5}$ phase, which is stable in very narrow compositional range, has been obtained mainly in a metallurgical way in the form of bulk crystals [2]. Its properties [3], like a high hardness ($H_V$ = 8-10GPa), a Young's modulus reaching that of steel (210GPa), a low dry friction coefficient measured against a diamond counterpart ($\mu$ = 0.02-0.2), a low thermal conductivity (~2$Wm^{-1}K^{-1}$) and exceptionally low surface energy (~20mJ/$m^2$), made this quasicrystalline phase the object of an increasing interest. However, all these results originate from measurements on bulk crystals with a low level of structure imperfections [4-8].

The high brittleness of quasicrystalline materials is an important factor limiting their applications in the bulk form. For this reason, numerous, mainly PVD techniques have been used to deposit them as thin films. AlCuFe thin film coatings have already been deposited by alloy/pressed powder target, single source magnetron sputtering [9], the sequential, multilayer sputter deposition of elemental sub-layers followed by high temperature post treatment [10], UHV electron beam sequential evaporation from elemental targets with post-annealing [11-13], and nano-, pico- as well as femto-second pulsed laser ablation (PLD) from alloy targets [14]. Besides the composition and structure studies, some of them have been characterised in terms of their mechanical and tribological properties [10, 15-17]. However, these studies refer to different tribo-test conditions and counterpart materials, which makes comparison attempts very questionable.

To gain knowledge on the deposition conditions and corresponding properties of such coatings, we deposited AlCuFe thin films using a multisource, magnetron co-sputtering system and studied their chemical and phase composition, structure as well as the basic mechanical (microhardness) and tribological (dry friction) properties in atmospheric conditions.

## 1. Experimental procedure

Thin film coatings of the AlCuFe type have been deposited by means of multisource, DC magnetron co-sputtering on (100) silicon wafers and 4H13 steel substrates of 28 mm in diameter. Steel substrates, quenched and tempered to the hardness of 5.3 GPa, have been mirror polished to $R_a < 70$ nm.

The technological chamber, pumped down to the ultimate pressure lower than $10^{-3}$ Pa by classical diffusion pump system, was equipped with three 2 inch, planar magnetron guns. Metallic Al, Cu and Fe targets of 4N purity have been sputtered simultaneously in pure Argon (5N) atmosphere at the pressure of 0.5 Pa. The rotated (60 rpm) sample holder, resistively heated up to 400°C, was placed in the confocal point of three magnetron guns, at the distance of 60 mm from each gun. During deposition, substrates were kept at the floating potential of about -10 V.

Power dissipated at each gun was duly controlled to obtain the appropriate ratio of the deposition rates of components and thus the expected composition of the coating. The deposition rate – sputtering power calibration curves have been prepared to control the influence of individual target erosion and in the interaction of the guns of the deposition rate of every component.

The average thickness of the deposited coatings was 2 μm as measured for steel substrates by the Calotest method.

The composition of the coatings was controlled by Energy Dispersive Spectroscopy (EDS). X-ray diffraction of $Co_{K\alpha}$ radiation in classical Bragg-Brentano geometry was used for crystalline structure identification, whereas SEM and TEM provided information on the surface morphology and the cross-section of the film, respectively.

To study the concentration depth profiles of elements in the deposited films, the SIMS technique was applied. The 5keV $Ar^+$ ion beam with the incidence angle of $45^0$ was used for sample etching.

The microhardness of films has been measured using Vickers indentation method at the load changing from 0.05 to 1N. Each time, the film microhardness value was found from the fitting of indentation data points by the function proposed by Korsunski et al. [18].

Friction tests have been carried out at room temperature in ball-on-disc geometry using 10 mm alumina balls polished to $R_a < 50$ nm at the normal load of 1N and sliding speed 25 mm/s. The relative humidity of laboratory air during measurements was 45±5%. Low normal load was used to extract specific frictional response of the coating material and to avoid the coating failure due to contact stresses. At this stage of work, the adhesion of coatings was not tested.

## 2. Results and discussion

The composition of deposited films was found as an average of EDS measurements at 5 points randomly chosen at the sample surface. The scattering of these values was less than 1 at. % and confirmed good homogeneity of coatings.

Thin films with a large excess of aluminium, sample 31 in the Fig. 1a, grow in the form of large crystallites of an unidentified phase. An increase of the copper content leads to the refinement of these crystallites (Fig. 1b), and finally to smooth surface of the film (sample 36) with the composition close to ψ-$Al_{62.5}Cu_{25.0}Fe_{12.5}$ phase (Fig. 1c).

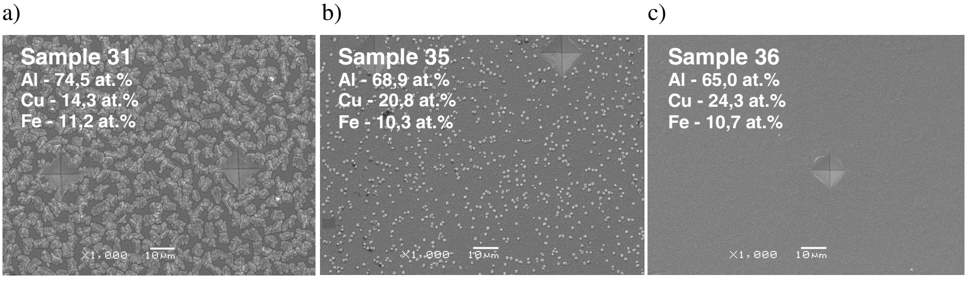


Fig. 1. SEM top view of as-deposited films with the composition approaching ψ-$Al_{62.5}Cu_{25.0}Fe_{12.5}$ phase stability region

Theq points at the composition triangle shown in the Fig. 2 are distributed at the area covering only a few atomic percent deviations from ψ-phase composition. Some of them are situated out of ψ-phase stability region entering β and λ phase neighbouring areas.

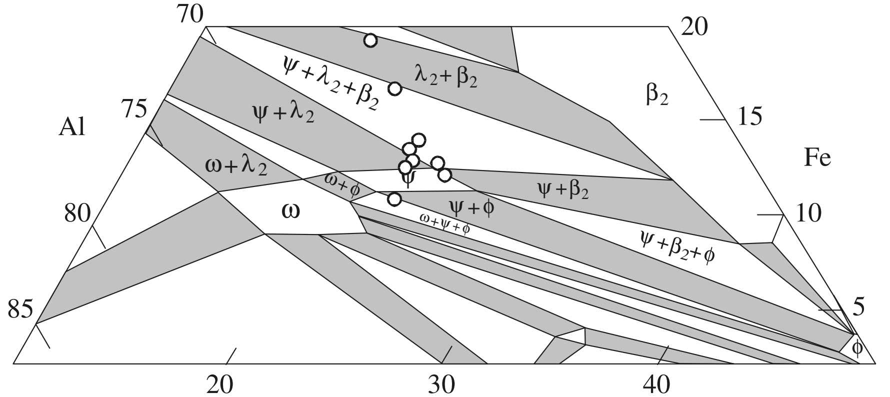


Fig. 2. The room temperature cross section of Al-Cu-Fe phase diagram showing the distribution of sample points around the ψ-phase stability region [19]

The X-ray diffraction analysis shows that, in the coatings deposited at 400°C, the cubic β phase is a dominant one, provided that the composition is close to the ψ-phase stability region (Fig. 3).

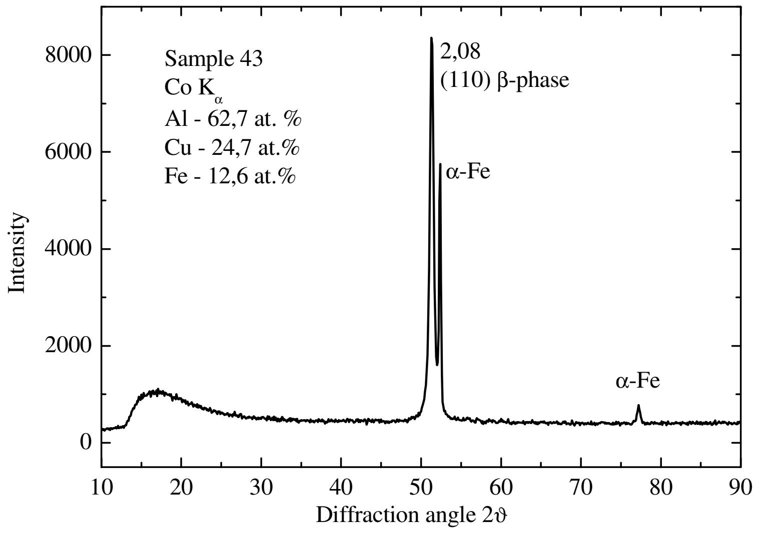


Fig. 3. The diffraction pattern of as deposited AlCuFe thin film sample with dominating β-Al(Fe,Cu) phase

The TEM cross section of such films, shown in Fig. 4, reveals the pronounced columnar structure of the coating. The diameter of columns is about 100 nm.

An increase of the iron content leads to the appearance of the λ phase. In both cases, the deposits are highly textured and only two prominent peaks of both phases are observed. Positions of these peaks are slightly shifted with respect to the mother phases (β-AlFe and λ-Al13Fe4) due to copper incorporation.

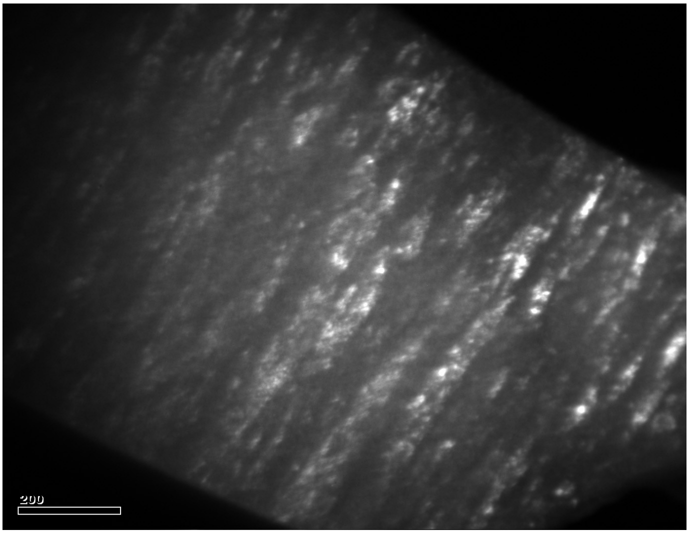


Fig. 4. TEM picture of as deposited AlCuFe thin film cross section

Annealing of films deposited at steel substrates and possessing the composition falling into ψ-phase stability region was undertaken to transform them into the desired icosahedral phase or at least initiate its nucleation. Unfortunately, annealing at 630°C under high vacuum conditions leads to diffusion of iron and chromium to the coating. Enrichment of the film with iron promotes nucleation of the λ phase instead of the expected icosahedral one. Evolution of diffraction patterns after the subsequent annealing steps have been shown in Fig. 5.

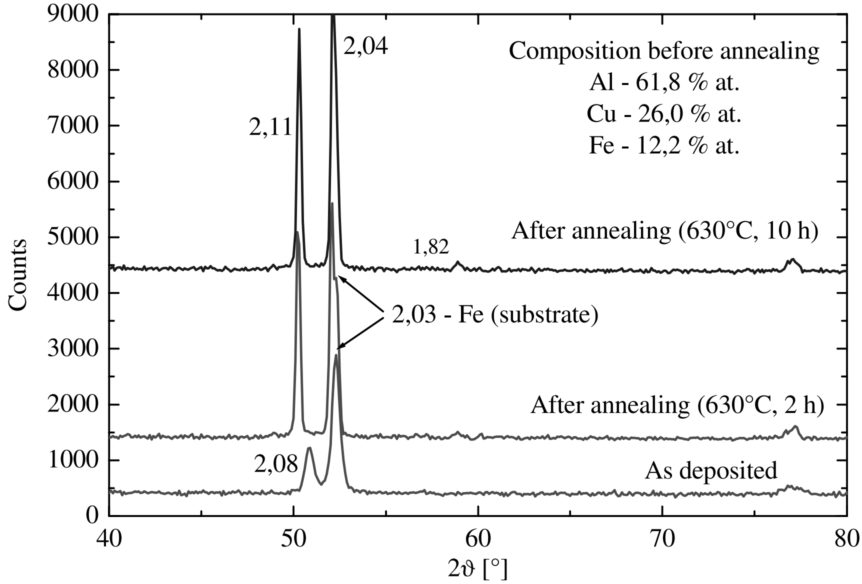


Fig. 5. Evolution of diffraction patterns after annealing of the coating with the initial composition close to the one of the ψ-phase

This conclusion is supported by the results of SIMS analysis showing the depth profiles of coating constituents after annealing (Fig. 6). The concentration gradient of iron and chromium can easily be observed.

Studies of mechanical and tribological properties have been performed on the deposited coatings, containing mainly the cubic β-phase with the composition close to the desired one, i.e. $Al_{62.5}Cu_{25.0}Fe_{12.5}$.

Microhardness measurements revealed a broad maximum at the film composition close to the one of the icosahedral phase as shown in Fig. 7. The microhardness value, reaching 8.5 GPa is also similar to the one reported for the ψ-phase bulk samples [3].

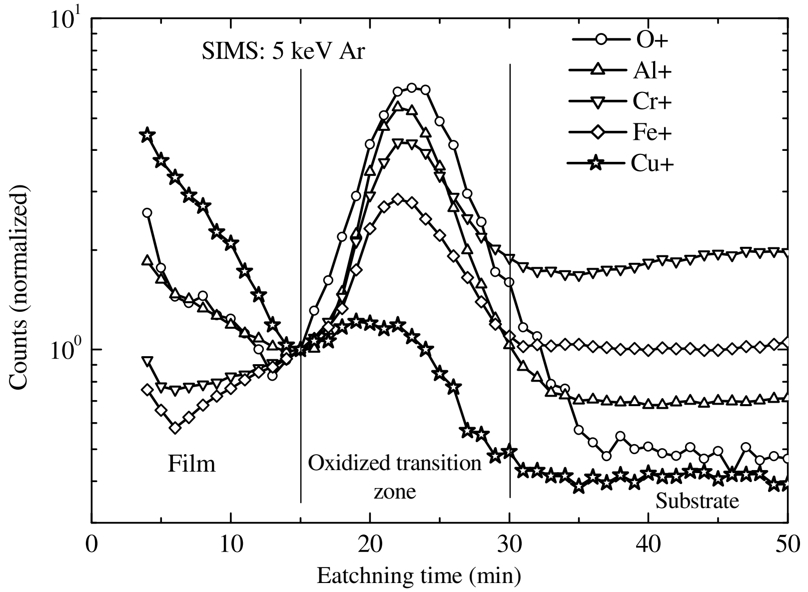


Fig. 6. The SIMS depth profile of AlCuFe thin film coating after 10 hours of annealing at 630°C

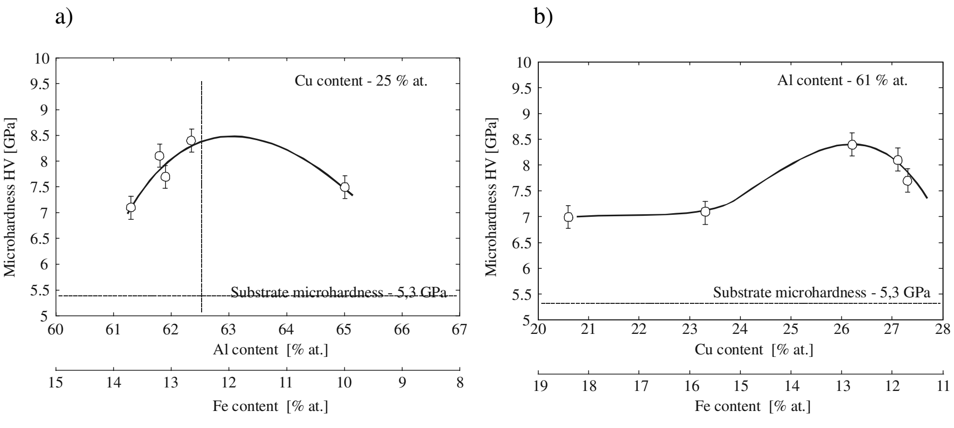


Fig. 7. The microhardness of the coating vs. the composition for constant: a) Cu and b) Al content

This trend could be considered as a signature of precipitation hardening induced by nucleation of the icosahedral phase. However, this supposition cannot yet be supported by diffraction or TEM observations.

Tribological tests carried out on the same samples do not show any pronounced trend. The friction coefficient values shown in Fig. 8 have been plotted versus the deviation of sample composition denoted as XYZ from the

$Al_{62.5}Cu_{25.0}Fe_{12.5}$ point. This deviation value has been calculated according to the formula: $|62.5 - X| + |25.0 - Y| + |12.5 - Z|$ [at.%].

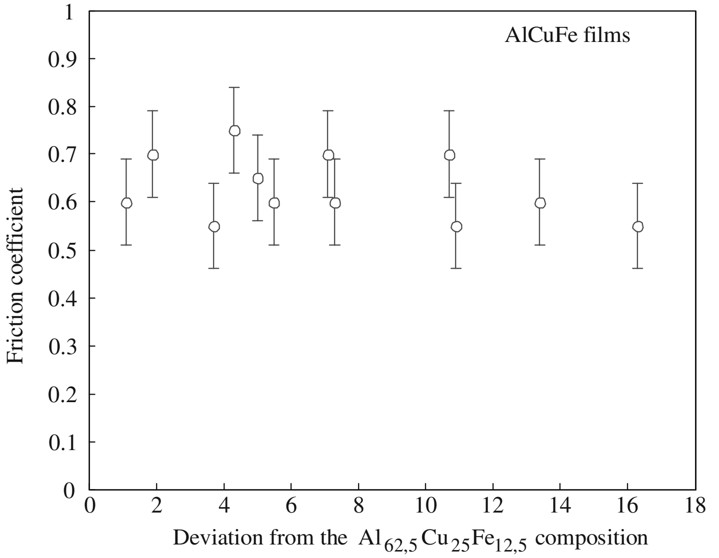


Fig. 8. The friction coefficient vs. the deviation of sample composition from $Al_{62.5}Cu_{25.0}Fe_{12.5}$ point

Registered friction coefficient values oscillate around 0.6±0.1, i.e. slightly below 0.8 observed for uncoated steel tested in the same conditions. Similar results of friction measurements on the cubic β-phase thin film coatings deposited by the magnetron sputtering of elemental powder pressed targets have been reported by Philips et al. [17]. The friction is, however, accompanied by relatively high wear, resulting in coating failure after about 2000-3000 cycles.

## Conclusions

AlCuFe thin film coatings have been deposited at 400°C on steel substrates by multi-source, DC magnetron sputtering from metallic targets. The structure of films is built of columns of about 100 nm in diameter. For films with the composition close to $Al_{62.5}Cu_{25.0}Fe_{12.5,}$ the cubic β-phase is a dominant one. An increase in the iron content, intentionally introduced during deposition or diffusing from the steel substrate during high temperature annealing, leads to the appearance of λ-$Al_{13}(FeCu)_4$ phase in the studied coatings.

The Vickers microhardness of the deposited films reaches a broad maximum of 8.5 GPa for coatings with the composition close to the icosahedral, quasicrystalline ψ-phase, which however has not been found in deposits.

Nanometric precipitation of this hard phase can be, however, considered as a cause of observed hardening.

The dry friction coefficient value, measured against alumina ball, oscillates around 0.6 and is similar to that observed by other authors for β-phase thin films.

The aim of further studies, which are still necessary, is to optimise deposition and, particularly, thermal post treatment conditions, to obtain films containing a controlled amount of the quasicrystalline phase and thus enhanced hardness as well as wear resistance.

## Acknowledgements

*Scientific work financed by the Ministry of Science and Higher Education and carried out within the Multi-Year Programme "Development of innovativeness systems of manufacturing and maintenance 2004–2008".*

The authors would like to express their thanks to Dr Jerzy Morgiel from the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences in Krakow for TEM studies, Dr Piotr Konarski and his co-workers from Industrial Institute of Electronics in Warsaw for SIMS analysis and Mr Paweł Kochamański from the Technical University of Szczecin for EDS composition studies. The help of Mr Zbigniew Kukliński and Mr Jan Kwiatkowski from Technical University of Koszalin in microhardness and X-ray diffraction measurements is also appreciated.

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## Struktura i właściwości cienkich warstw międzymetalicznych Al-Cu-Fe nanoszonych metodą wieloźródłowego rozpylania magnetronowego

**Słowa kluczowe**

Rozpylanie magnetronowe, cienkie warstwy, fazy międzymetaliczne, układ Al-Cu-Fe, właściwości tribologiczne.

**Streszczenie**

Cienkie warstwy trójskładnikowe Al-Cu-Fe nanoszono metodą stało-prądowego, wieloźródłowego rozpylania magnetronowego z katod metalicznych. Skład warstw, kontrolowany metodą spektroskopii energodyspersyjnej (EDS) był zbliżony do składu quasi-krystalicznej fazy $\psi$-$Al_{62.5}Cu_{25.0}Fe_{12.5}$ o symetrii dwudzie-stościanu. Struktura warstw nanoszonych przy temperaturze podłoża równej 400°C odpowiadała kubicznej fazie $\beta$-Al(Cu,Fe). Morfologię powierzchni warstw oraz ich strukturę badano odpowiednio metodami elektronowej mikroskopii skaningowej (SEM) oraz transmisyjnej mikroskopii elektronuzji składniowej (TEM).

Długotrwałe wygrzewanie badanych warstw, nanoszonych na stali prowadzi do dyfuzji żelaza w głąb warstwy, co skutkuje pojawieniem się bogatej w żelazo jednoskośnej fazy $\lambda$-$Al_3Fe_{1-x}Cu_x$. Wstępne badania mikro-twardości wskazują na szerokie maksimum na poziomie 8,5 GPa dla warstw o składzie zbliżonym do składu fazy quasi-krystalicznej. Obecność wydzieleń tej fazy w badanych warstwach nie została jeszcze jednoznacznie potwierdzona. Współczynnik tarcia, mierzony względem ceramiki alundowej w układzie kula–płaszczyzna, oscyluje wokół wartości 0,65 i jest niższy niż obserwowany dla nie-pokrytej stali 4H13.