

## ROOM TEMPERATURE DEFORMATION OF IN-SITU GROWN QUASICRYSTALS EMBEDDED IN AL-BASED CAST ALLOY

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### Abstract

An Al-based cast alloy containing Mn, Be and Cu has been chosen to investigate the room temperature deformation behavior of QC particles embedded in Al-matrix. Using LOM, SEM (equipped with EDS), conventional TEM with SAED and controlled tensile and compression tests, the deformation response of AlMn<sub>2</sub>Be<sub>2</sub>Cu<sub>2</sub> cast alloy at room temperature has been examined. Alloy consisted of Al-based matrix, primary particles and eutectic icosahedral quasicrystalline (QC i-phase) and traces of  $\Theta$ -Al<sub>2</sub>Cu and Al<sub>10</sub>Mn<sub>3</sub>. Tensile and compression specimens were used for evaluation of mechanical response and behavior of QC i-phase articles embedded in Al-cast alloy. It has been established that embedded QC i-phase particles undergo plastic deformation along with the Al-based matrix even under severe deformation and have the response resembling that of the metallic materials by formation of typical cup-and-cone feature prior to failure. So, we can conclude that QC i-phase has the ability to undergo plastic deformation along with the Al-matrix to greater extent contrary to e.g. intermetallics such as  $\Theta$ -Al<sub>2</sub>Cu for instance.

Keywords: Aluminium alloys, Quasicrystals (QCs), Compression and tensile tests

### Introduction

For the past twenty years, since their discovery in 1984, quasicrystals (QCs) have been focus of intense studies because of their unique physical properties [1]. There have been, and still are, research efforts for finding an application niche for QCs. Namely, QCs constitute additional state of matter to that of crystalline and glassy. They exhibit, due to their unique cluster-like structure, physical properties that deviate from those known in crystals, amorphous materials and intermetallics or ceramics [2]. QCs are known to form in many metallic systems [3, 4] but only those with lower melting points

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have the potential to see use in structural applications. Having that in mind, the Al-based QCs forming alloys are the ones that deserve attention as they can be optimized and processed to provide a hierarchy in microstructure which can ensure very good mechanical properties [5, 6]. Mechanical properties of metallic materials are generally related to the ability or inability of dislocations to slide and climb, i.e. to their mean free path and then depend on twinning capability of particular metal or alloy, grain size etc. QCs represent yet another novel hardening mechanism, moreover as they can form in a number of Al-based systems [7-10] with the Al-Mn being one of the first systems to exhibit ability to form QCs [11].

### Theoretical background

Alloys from the Al-Mn-Be-(Cu) system were chosen as they are proven to provide larger amounts of QC  $\epsilon$ -phase embedded in the aluminum-based matrix only if the cooling rates are sufficiently high, i.e. exceeding a few  $100 \text{ K s}^{-1}$  [10]. In this respect it is very important to choose the most appropriate chemical composition to ensure the predominant formation of QC phases and thus lower the content of beryllium. Optimization of the chemical composition of alloys from the Al-Mn-Be-Cu system requires profound knowledge on the thermodynamic equilibrium in quaternary alloys which solidify in non-equilibrium conditions. As Al-Mn-Be-Cu quaternary system is not yet known, one has to rely on open literature data related to the Al-Mn-Cu, Al-Cu-Be and Al-Mn-Be ternary systems, Fig. 1. As QC phases in general have properties very different to those of crystalline state alloys, many attempts have been made in the recent past to use QC phases as reinforcement for the ductile aluminum-based matrix [4]. Moreover, some alloys have shown the ability to form large amounts of QC phases during solidification of molten alloys in a fashion typical for so-called *in-situ composites*.

Constitution of these systems indicates a complicated solidification course in equilibrium conditions and even more so, when higher cooling rates needed for the QC phases to form, are employed [12, 13]. Nevertheless, at least two out of three ternary systems have eutectic point in Al-rich corner which implicates the possibility of heterogeneous eutectic-like structures to form during solidification even in quaternary alloys [14, 15]. This is most beneficial as it allows one to fabricate *in-situ composite* materials that exhibit very good cohesion between matrix and parent reinforcing component which in our case is a QC phase.

Although there is a lot known about the deformation of single QCs [16, 17], especially at elevated temperatures, there were only few attempts made to use QC particles as a reinforcement of alloys for structural applications. There are many ways in which QC particles can be introduced into alloys such as mechanical alloying, powder metallurgy, injection, infiltration etc. Authors have recently shown that Al-Mn-Be-Cu cast alloys can reach ultimate tensile strengths and rates of deformation comparable to Al-alloys of 2XXX series without consecutive heat treatment [5]. Thus, QCs could see wider use in structural applications if a simple and cost-effective way of producing high-strength light-weight alloys either based on aluminum or magnesium could be devised.

One of the goals in presented work was to examine the deformation behavior of *in-situ* grown QC particles, by means of modern investigation techniques available, when severe deformation is used.

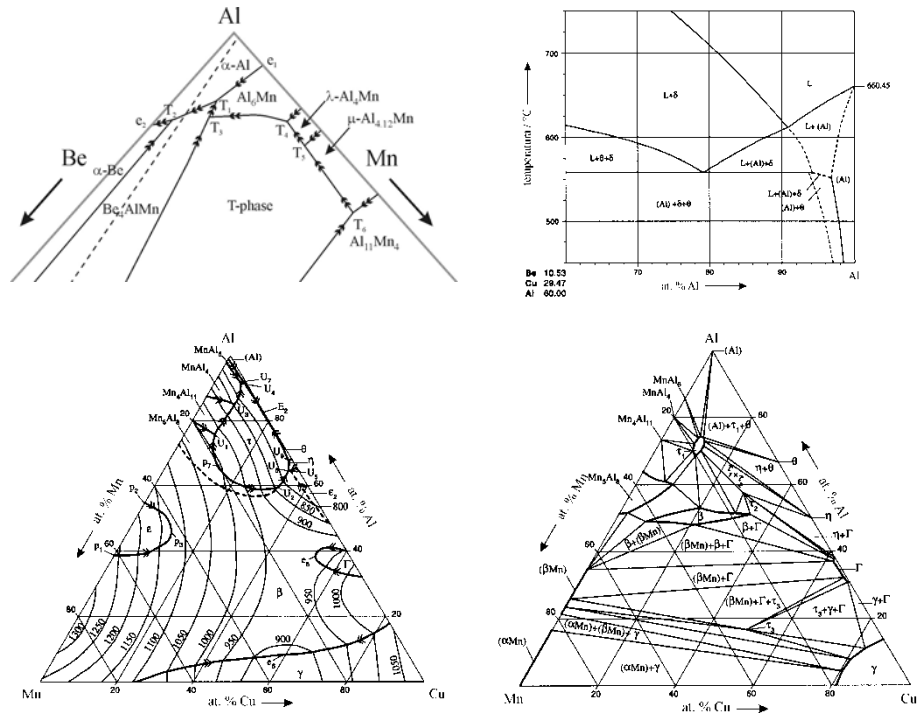


Fig. 1. Ternary systems related to quaternary Al-Mn-Be-Cu alloy: (a) Al-rich corner in Al-Mn-Be ternary system, (b) vertical section through Al-Be-Cu ternary system at Cu:Be=20:1 and (c) liquidus surface and (d) isothermal section at 293 K in Al-Mn-Cu ternary system [14,15].

**Experimental work**

For the synthesis of examined alloy from the Al-Mn-Be-Cu system pure elements (Al 99.99%, Mn 99.9% and Cu with 99.99 %) and a masteralloy AlBe5 have been used. Conventional electric heated furnace was employed to cast the melt into permanent copper casting mould which ensured controlled high cooling rates for the QC i-phase to form. Permanent casting mold with four casting troughs of different diameters (2.5, 4, 6, 10 and 16 mm) was designed to provide different cooling rates. Chemical composition of the examined alloy after the casting was checked by ICP—AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy), and is given in Table 1.

Table 1. Chemical composition of synthesized Al-Mn-Be-Cu alloy

	Al	Mn	Be	Cu
Mass %	87.40	8.60	0.5	3.50
At. %	92.30	4.50	1.6	1.6

The constitution of synthesized alloy has been examined by light optical microscopy (LOM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and selected area electron diffraction (SAED). For the purpose of

LOM and SEM investigations specimens were prepared using conventional metallographic route. This would involve grinding, polishing and etching (aqueous NaOH) for the LOM, while samples for the SEM were left non-etched. Thin foil samples were stamped out and ion polished for perforation on GATAN PIPS 691 for the TEM (AEM JEOL 2000, JEOL JEM 3010) and HREM (JEOL 2010F) examination. ZWICK 250 was used for tensile tests and GLEEBLE 1500D was employed for compression testing.

### Results and Discussion

Based on previous experiences of authors with preparation and examination of morphology of QCs these phases or particles could be distinguished from all other phases present in the microstructure only by means of LOM and SEM. QCs feature symmetry elements, forbidden in crystals structures, i.e. 5-, 10- or 12-fold elements, also affects their appearance on the micro-level. Namely, QCs often appear in a form of pentagonal- or trigonal-like forms that are easily distinguished from other usually intermetallic phase which feature irregular shapes and forms.

Cast bars with different diameters were examined by LOM and SEM to assess the constitution and establish the amount, distribution and shape of the QC i-phase. Fig. 2 presents the microstructure of the investigated alloy, consisting of Al-matrix ( $\alpha_{Al}$ ), QC i-phase (as primary phase and within heterogeneous structure ( $\alpha_{Al}$ +i-phase)) and traces of interdendritic  $Al_2Cu$  for all four diameters.

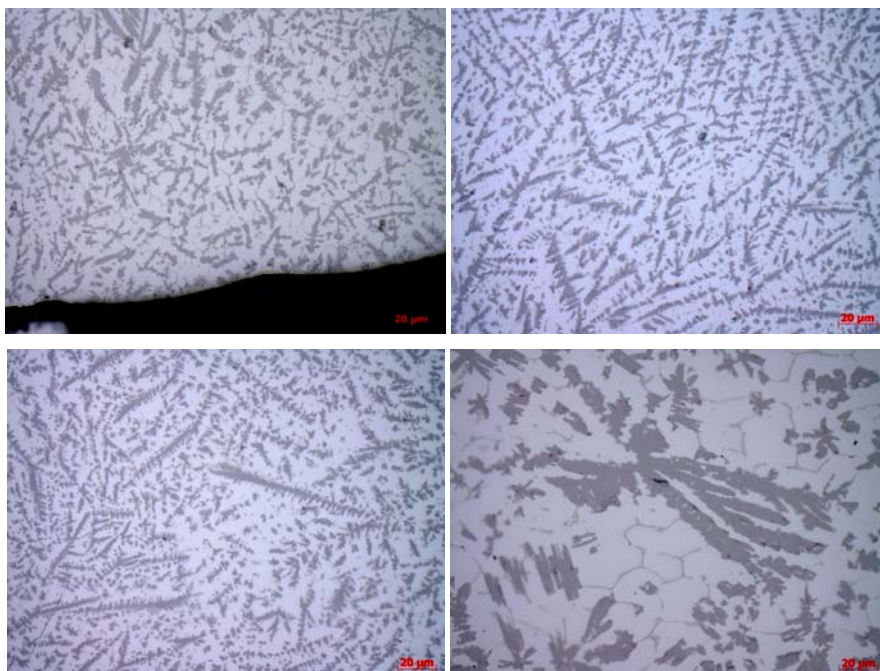


Fig. 2 LOM analysis of as-cast microstructure of AlMn4Be2Cu2 alloy: (a) 2.5 mm, (b) 4 mm, (c) 6 mm and (d) 10 mm diameter; QC i-phase is dominant next to  $\alpha_{Al}$  and traces of  $\Theta-Al_2Cu$ .

Detection of beryllium in SEM, based on the EDS spectra alone, was virtually impossible which also impaired ability to confirm which particles could be ascribed to the QC i-phase, Fig. 3. Since  $\theta$ -Al<sub>2</sub>Cu phase has particular morphology in Al-based alloys and yields high contrast in the BSE mode of the SEM, this phase could be unambiguously distinguished from all the others. Nevertheless, based on previous research efforts devoted to the reliable detection of the QC i-phase, accurate distinction and assessment of the amount of QC i-phase in AlMn<sub>4</sub>Be<sub>2</sub>Cu<sub>2</sub> alloy could be also made [18-22].

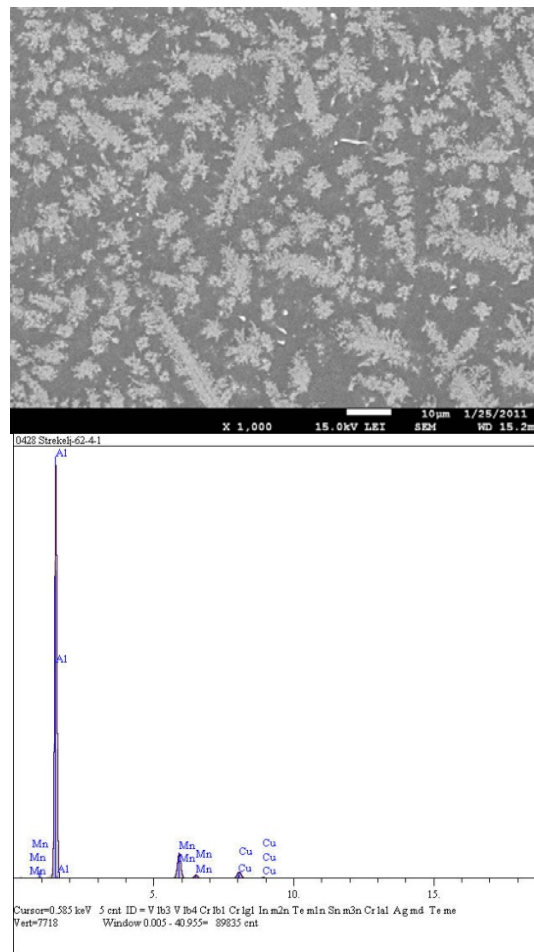
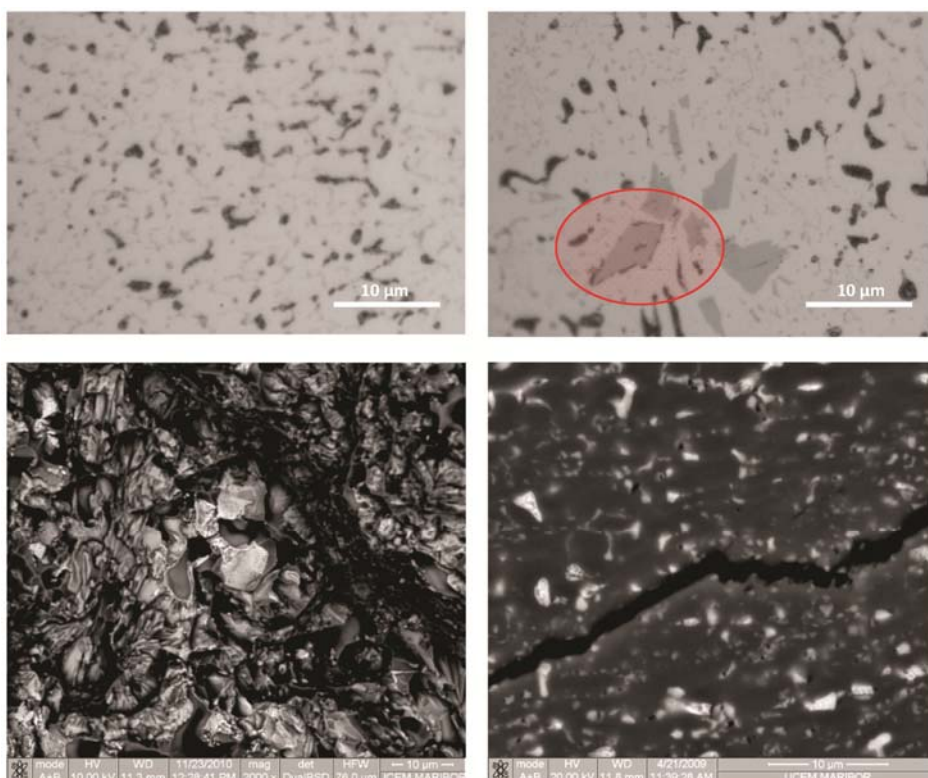


Fig. 3. SEM analysis of as-cast microstructure in AlMn<sub>4</sub>Be<sub>2</sub>Cu<sub>2</sub> alloy: (a) BSE image of 4 mm diameter bar and (b) accompanying spectra.

In general, the formation of the QC i-phase was not possible with usual cooling rates (under 100 Ks<sup>-1</sup>), then higher cooling rates achieved through casting of thinner diameters of a permanent mold made of copper had to be applied. This ensured cooling rates of approximately 500 Ks<sup>-1</sup> needed for QC i-phase to form in large amounts. Having achieved this intermediate milestone it could be proceeded with mechanical

testing and investigation of post-deformed structure of QC i-phase embedded in Al-Mn-Be-Cu cast alloy.

Compression tests registered 0.9 of true strain up to 450 MPa of true stress for 2 and 4 mm diameter, whilst thicker diameter (smaller amount of QC i-phase) gave values of 0.4 for true strain and around 400 MPa for true stress. Tensile tests provided similar results with ultimate tensile stress close to 400 MPa and elongation of 9.0 % for both 2 and 4 mm samples. Fractured surface from a tensile specimen is showing evidence of plastic fracture with spots where QC i-phase particles were embedded, Fig. 4.



*Fig. 4. Analysis of microstructure after tensile and compression test: in-situ deformation of QC i-phase particles along with Al-matrix (a, LOM) and detachment (red oval) of  $Al_{10}Mn_3$  intermetallic from the parent Al-matrix (b, LOM), fractured surface of the tensile probe with evidence of plastic deformation (c, SEM) and crack propagation mainly through the matrix where most of the micro-constituents also underwent deformation. Occasionally the crack propagation was assisted by the breaking and decohesion of intermetallic particles of  $Al_{10}Mn_3$  phase (d, SEM).*

TEM/HREM analysis of samples made from specimens deformed during tensile tests proved to be very demanding in interpretation of results. Nevertheless, authors were able to show that QC i-phase deformed along with the Al-based matrix maintains cohesion of the interphase boundary, Fig. 5.

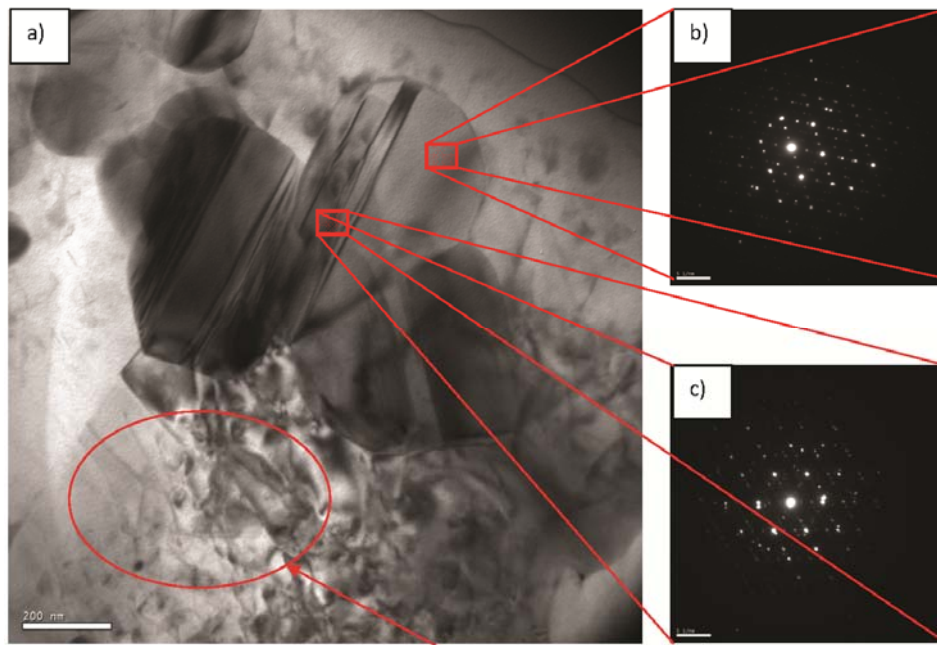


Fig. 5. TEM analysis of QC i-phase after deformation during tensile test: large QC i-phase particles exhibiting “plane-like” defects while Al-matrix features high dislocation density (a), SADP with 3-fold axis of non-deformed part of QC i-phase (b) and SADP of deformed part of QC i-phase with additional major diffraction spots (c).

Al-based matrix in the Fig. 5a shows a heavily deformed area full of inter-tangled dislocations typical for non-homogeneous deformation whilst QC i-phase particles exhibit homogeneous deformation. Most important is the fact that QC i-phase particles did not crack to form voids like intermetallic particles do and they maintained total cohesion with parent Al-matrix. In this case QC i-phase can obviously undergo severe deformation without breaking into smaller pieces causing formation of voids when embedded in metallic matrix. As QC i-phase are generally much harder [18] than the parent Al-matrix, the embedded QC i-phase will harden the alloy. This was also the case with our synthesized alloy.

### Conclusions

LOM and SEM analyses have shown that Al-Mn-Be-Cu alloys with embedded QC i-phase are deformable and that QC i-phase particles underwent plastic deformation along with the parent Al-matrix. Decohesion on the interphase boundary between particles and Al-matrix was in all cases associated with intermetallics found in the alloy, i.e.  $\text{Al}_2\text{Cu}$  and  $\text{Al}_{10}\text{Mn}_3$  and not with QC i-phase. Examination of deformed samples with TEM/SAED showed planar-like defects in QC i-phase particles due to severe deformation during tensile and compression tests. All these shows that QC i-phase could potentially be used as reinforcing micro-constituent for some Al-based alloys used for structural applications.

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### References

- [1] Quasicrystals, Structure and Physical Properties. Edited by Hans-Rainer Trebin: Wiley-VCH GmbH & Co. KgaA, Weinheim, 2003.
- [2] K.F. Kelton, *Int. Mat. Rev.*, vol. 38 no. 3 (1993) 105-137.
- A. Inoue, H. Kimura, *JLM* 1 (2001) 31-41.
- [3] F. Schurack, J. Eckert, L. Schultz, *Acta mater.* 49 (2001) 1351-1361.
- [4] B. Markoli, T. Bončina, F. Zupanič, *Mater. wiss. Werkst. tech.*, vol. 43 no. 4 (2012) 340-344.
- [5] F. Zupanič, T. Bončina, N. Rozman, B. Markoli, *RMZ-mater. geoenviron.*, vol. 58 no. 1 (2011) 1-14.
- [6] S.V. Divinski, *Scripta mater.* 34 (1996) 1351-1355.
- [7] G.S. Song, E. Fleury, S.H. Kim, W.T. Kim, D.H. Kim, *J. Alloys Compd.* 342 (2002) 251-255.
- [8] S.H. Kim, G.S. Song, E. Fleury, K. Chattopadhyay, W.T. Kim, D.H. Kim, *Philos. mag.*, A 82 (2002) 1495-1508.
- [9] D. Vojtech, K. Saksl, J. Werner, B. Bartova, *Materials Science and Engineering A* 428 (2006) 188-195.
- [10] D. Shechtman, I. Blech, D. Gratias, J. W. Cahn, *Phys. Rev. Lett.* 53 (1984) 1951-1953.
- [11] T. Bončina, B. Markoli, F. Zupanič, *Metalurgija (Sisak)*, no. 2 vol. 51 (2012) 167-174.
- [12] B. Markoli, T. Bončina, F. Zupanič, *Croat. chem. acta*, vol. 83 no. 1 (2010) 49-54.
- [13] F. Zupanič, B. Markoli, I. Naglič, T. Bončina, *J. Alloys Compd.* 570 (2013) 125-132.
- [14] F. Zupanič, B. Markoli, I. Naglič, T. Weingärten, A. Meden, T. Bončina, *Microsc. Microanal.* 19, (2013) 1308-1316.
- [15] M. Feuerbacher, P. Schall, Y. Estrin, Y. Brechet, *Philos. mag. lett.*, vol. 81, iss. 7, (2001) 473-482.
- [16] M. Feuerbacher. Dislocations in icosahedral quasicrystals, *Chem. Soc. rev.*, vol. 41, iss. 20, (2012) 6745-6759.
- [17] T. Bončina, M. Čekada, B. Markoli, F. Zupanič, *J. alloys compd.*, vol. 505 iss. 2 (2010) 486-491.
- [18] T. Bončina, B. Markoli, F. Zupanič, *J. Microsc. (Oxf.)*, vol. 233 no. 3 (2009) 364-371.
- [19] F. Zupanič, T. Bončina, A. Križman, W. Grogger, C. Gspan, B. Markoli, S. Spaić, *J. alloys compd.*, vol. 452 iss. 2 (2008) 343-347.
- [20] F. Zupanič, T. Bončina, B. Šuštaršič, I. Anžel, B. Markoli, *Mater. charact.*, vol. 59 no. 9 (2008) 1245-1251.
- [21] F. Zupanič, T. Bončina, N. Rozman, I. Anžel, W. Grogger, C. Gspan, F. Hofer, B. Markoli, *Z. Kristallogr.*, 223 (2008) 735-738