

FA2-MS13-P07

Coherent scattering domain measurements in Al-Cu-Fe alloys during in-situ heating. Carmen Mihoc^a, Manuela Stir^b, Eberhard Burkel^a. ^aUniversity of Rostock, Institute of Physics, Germany. ^bEMPA, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland.

E-mail: carmen.mihoc@uni-rostock.de

Al-Cu-Fe quasicrystalline alloys were recently developed as bulk amorphous advanced materials with high potential for applications like high-temperature thermal barriers, low-friction and wear-resistant coatings [1-4], composite biomaterials [5] or catalysts [6]. The crystallization of as-prepared alloys plays a crucial role in the technological application of these new materials. The nucleation and growth of nanoscale phases in these alloys during constant rate heating was investigated using high-resolution high-temperature powder X-ray diffraction.

A series of nanocrystalline Al-based alloys were synthesized by mechanical alloying. The temperature stability of the Al-Cu-Fe alloy was investigated by in-situ angular-dispersive X-ray diffraction at the B2 high-resolution diffractometer at HASYLAB. Constant heating rate annealing experiments were performed in inert gas atmosphere in order to analyse the evolution of phase constituents. The X-ray diffraction (XRD) patterns ($\lambda = 0.65125 \text{ \AA}$) were collected in transmission mode during heating up to 800°C. The formation of the single icosahedral quasicrystalline ψ -phase is the main crystallization event. The temperature dependence of the average coherent scattering domains was obtained using the Scherrer equation. Further analysis of the diffraction pattern are in progress, with the aim to resolve the temperature evolution of strain during constant rate heating and the crystallization kinetics.

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Keywords: quasicrystals, X-ray diffraction, solid-state phase changes

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In-situ Neutron Diffraction Measurement on Co-Re Alloys at High Temperature. Debashis Mukherji^a, Pavel Strunz^{b,c}, Ralph Gilles^d, Michael Hofmann^d, Markus Hölzel^d, Joachim Rösler^a. ^aTechnische Universität Braunschweig, IfW, Germany. ^bNuclear Physics Institute, Řež near Prague, Czech Republic. ^cResearch Center Řež, Řež near Prague, Czech Republic. ^dTechnische Universität München, FRM II, Germany.

E-mail: d.mukherji@tu-bs.de

Co-Re-based alloys are being developed at the TU-Braunschweig to supplement Ni-base superalloys at very high temperatures (1200°C) in gas turbine applications [1]. These alloys are strengthened by various carbides ($M_{23}C_6$ and MC types). Additionally, topologically close packed \square phase may also be stable in the alloys. Pure Co exists in two allotropic forms: as hcp \square and fcc \square structures and the high temperature

phase is metastable at room temperature (RT) [2]. Re addition stabilizes the \square phase at RT and therefore a hcp \rightarrow fcc phase transformation occur on heating the alloy. Using in-situ neutron diffraction measurements at Stress Spec and SPODI (FRM II) we monitored this transformation in two Co-Re-base alloys CoRe-1 (Co-17Re-23Cr-2.6C) and CoRe-2 (Co-17Re-23Cr-1.2Ta-2.6C) during heating and cooling in the temperature range 1100° and 1300°C. The reversible hcp \rightleftharpoons fcc transformation shows a large hysteresis (100K). On heating the transformation start and end at the same temperatures in both CoRe-1 and CoRe-2, but the reverse transformation occurs at different temperature ranges for the two alloys and the transformation lag behind by $\sim 25^\circ\text{C}$ (lower temperature) in CoRe-2. The Cr_{23}C_6 carbide and the \square phase play critical role in the phase transformation, but the TaC remains stable.

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Keywords: superalloys, neutron diffraction, phase transitions

FA2-MS13-P09

Binary Lanthanum Stannides: LaSn_2 , La_2Sn_5 , La_3Sn_7 , LaSn_3 . Michael Schwarz, Ines Dürr, Caroline Röhr. Institut für Anorganische und Analytische Chemie, University of Freiburg, Germany.

E-mail: michis@hematite.chemie.uni-freiburg.de

In the course of our systematic studies on lanthanum triel/tetrel-ides the known binary lanthanum stannides were synthesized and structurally reinvestigated [1]. The structure types of LaSn_2 (NdSn₂ type), La_3Sn_7 (Ce_3Sn_7 type), La_2Sn_5 (Ce_2Sn_5 type) have only been assigned from powder data by comparison with the isostructural rare earth compounds, which are of note due to their magnetic properties [2, 3]. The title compounds were synthesized by arc-melting stoichiometric amounts of the elements. Their structures were refined by the means of X-ray powder Rietveld methods (La_2Sn_5 : *Cmmm*, $a = 464.52(5)$, $b = 3582.7(3)$, $c = 469.53(6)$ pm, $R(F^2) = 0.086$, $R_p = 0.061$; La_3Sn_7 : *Cmmm*, $a = 458.93(11)$, $b = 2630.3(7)$, $c = 470.48(13)$ pm, $R(F^2) = 0.086$, $R_p = 0.061$; LaSn_3 : *Pm3m*, $a = 477.86(2)$ pm, $R(F^2) = 0.095$, $R_p = 0.111$). Whereas these three stannides crystallize with the primarily assigned structure types, LaSn_2 did not form the reported NdSn₂ type. Instead, the new high temperature form crystallizes with the hexagonal AlB_2 structure type. Starting from the corner-sharing Sn_6 -octahedra of the tin-rich compound LaSn_3 , the structures of La_2Sn_5 (triple octahedral blocks), La_3Sn_7 (double blocks) and LaSn_2 (single octahedral layers) can be topologically described by a successive shearing of the octahedral blocks. A more detailed crystal analysis, now possible on the basis of the full structural information, reveals isolated zig-zag-chains (shortest distance $d_{\text{Sn-Sn}} = 307.1(2)$ pm in La_2Sn_5) running along the shear vector, rather than

separated octahedral blocks. This new interpretation is verified by the results of FP-LAPW computational studies.

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Keywords: lanthanum stannides, Rietveld refinement, electronic structure

FA2-MS13-P10

Influence of low temperature aging on the crystalline structure of the carbon martensite Vasily Tarasov, Vitaliy Danilchenko, Viktor Iakovlev. *G. V. Kurdyumov Institute for Metal Physics, Kyiv, Ukraine.*

E-Mail: nothingface@mail.ru

Thermal stability of the α -martensite after cyclic γ - α - γ martensitic transitions was investigated using the x-ray method and single crystal specimens of two types of alloys: alloy 1 – Fe - 24,5 wt.% Ni - 0,5 wt. % C, alloy 2 – Fe - 9,7 wt. % Ni - 1,54 wt. % C. Specimens had the austenitic structure at room temperature. The direct γ - α transition occurred when cooling in liquid nitrogen. The reverse α - γ transition was realized by heating in salt bath up to 550 °C (alloy 1) and 700 °C (alloy 2) with the heating rate of 60 °C per second. Under such conditions the reverse α - γ transition was shear and diffusionless. The X-ray investigations were realized in rotating chamber RKV-86 with iron emission. Carbon α -martensite decomposition was observed by the change of the angular position (Bragg angle) of diffraction reflexes (200) _{α} and (002) _{α} and by the martensitic lattice tetragonality rate c/a change.

It was determined that the α -martensite formed in the austenite after γ - α - γ transitions decomposed more intensively. As a result, when heated up to 100 °C, the amount of depleted carbon of α -solid solution (χ -phase) in the alloy 1 raised up to 50 % relatively to its raising up to 20 % in the initial alloy. High carbon martensite of the alloy 2 decomposed with forming the only one carbon-depleted α -solid solution except the two in the initial alloy. The aged martensite of both alloys was depleted of carbon to a value close to its equilibrium concentration in α -Fe. This process ended as early as 80-120 °C.

The intensification of the carbon martensite decomposition after γ - α - γ transitions associated with the influence of crystalline structure defects which appear during direct γ - α and reverse α - γ transitions. The electron microscopic study shows the density of dislocations in reverted austenite is more than three orders bigger than in initial austenite. Moreover, additional subboundaries of disoriented fragments appeared. The martensite received these defects after reverse α - γ transition. As a result, the diffusion of carbon atoms on crystalline structure defects was enhanced. This caused the acceleration of the carbon α -solid solution decomposition.

Keywords: crystalline structure, X-ray crystal structure analysis, electron microscopy analysis

FA2-MS13-P11

A high-pressure study of Realgar. Daniel M. Többens, Raffaella Sagl, Clivia Hejny. *Mineralogy and Petrography, University of Innsbruck, Austria.*

E-mail: daniel.toebbens@uibk.ac.at

Realgar, chemical composition As₄S₄, is well known for its use as a red color pigment in painting and art for many centuries. In addition, it is a naturally occurring semiconductor, used in a number of optoelectronic applications. A natural sample from the "Baia Sprie" mine in Rumania was studied in a diamond anvil cell in order to analyze the behavior of Realgar under high-pressure conditions. Single crystal data could be obtained at pressures up to 5.4 GPa, powder data up to 43 GPa (ESRF/U. of Heidelberg, Miletich-Pawliczek R., Pippinger T., Ullrich A.). Electron microprobe analysis gave a composition close to ideal for this sample. For a deeper understanding of the experimental results DFT calculations were done using the software CRYSTAL06 [1], with Gaussian basis sets modeled as pseudo-potentials in DURAND-311G(1) and DURAND-3111G(1) contractions for sulfur and arsenic, respectively, and the generalized gradient approximation Perdew–Wang 92 (PWGGA). The structure of Realgar is characterized by cage-like molecules, oriented in rods parallel [100] and packed along [010]. The intra-molecular distances do not show a measurable shortening. Compression occurs mainly between the molecules, more precisely between the rods stacked along [010]. The compressibility was fittable by a Birch–Murnaghan equation of state, with resulting bulk modules $K_0 = 11.0(4)$ GPa, $K' = 9.0$ (from single crystal data) and $K_0 = 11.7(2)$ GPa, $K' = 7.8(1)$ (from DFT calculations up to 38 GPa). No phase transition was observed for the entire pressure range in spite of a compression to about 60% of the initial volume. During pressure increase, a continuous color change from yellow through red into black was observed. The color change is reversible on pressure decrease. UV-Vis spectroscopy (U. of Vienna, Wildner M.) showed this to be caused by a shift of the optical absorption edge to higher wavelengths with increasing pressure. It was assumed that this behavior is caused by a reduction of the direct band gap, and thus is a feature of the ideal crystal structure. Band gaps calculated by DFT methods are known to be too narrow generally. To overcome this problem simplified expansions according to the BZW-optimization process [2] were used to calculate the band structure. The values resulting from this were satisfactory, being only 15% smaller than the experimental ones. The calculated pressure dependency of the direct band gap is in full agreement with the experiment. Raman spectroscopy (U. of Vienna, Nasdala L.) revealed a general hardening of those vibrations associated with movements of the molecules as a whole. Vibrations associated with intra-molecular bending and stretching were affected less.

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FA2-MS13-P12

Neutron investigation of martensitic and superelastic shape memory NiTi wire. Michael Tovar. *Helmholtz-Zentrum Berlin (HZB) für Materialien und Energie, Berlin, Germany.*

E-mail: tovar@helmholtz-berlin.de