

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.*

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Thermal stability of the  $\alpha$ -martensite after cyclic  $\gamma$ - $\alpha$ - $\gamma$  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  $\gamma$ - $\alpha$  transition occurred when cooling in liquid nitrogen. The reverse  $\alpha$ - $\gamma$  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  $\alpha$ - $\gamma$  transition was shear and diffusionless. The X-ray investigations were realized in rotating chamber RKV-86 with iron emission. Carbon  $\alpha$ -martensite decomposition was observed by the change of the angular position (Bragg angle) of diffraction reflexes (200) <sub>$\alpha$</sub>  and (002) <sub>$\alpha$</sub>  and by the martensitic lattice tetragonality rate  $c/a$  change.

It was determined that the  $\alpha$ -martensite formed in the austenite after  $\gamma$ - $\alpha$ - $\gamma$  transitions decomposed more intensively. As a result, when heated up to 100 °C, the amount of depleted carbon of  $\alpha$ -solid solution ( $\chi$ -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  $\alpha$ -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  $\alpha$ -Fe. This process ended as early as 80-120 °C.

The intensification of the carbon martensite decomposition after  $\gamma$ - $\alpha$ - $\gamma$  transitions associated with the influence of crystalline structure defects which appear during direct  $\gamma$ - $\alpha$  and reverse  $\alpha$ - $\gamma$  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  $\alpha$ - $\gamma$  transition. As a result, the diffusion of carbon atoms on crystalline structure defects was enhanced. This caused the acceleration of the carbon  $\alpha$ -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.*

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Realgar, chemical composition As<sub>4</sub>S<sub>4</sub>, 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 (PW92). 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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**Keywords:** high pressure, ab-initio calculations, sulfides

#### 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.*

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Shape memory alloys like NiTi (*nitinol*) show a large field of applications, i.g. as flexible glass frames, surgical instruments or as actuators in robotic systems. The shape memory effect is based on the crystallographic phase transition of monoclinic martensite to cubic austenite. In this study NiTi wire [1] were investigated by neutron diffraction using the E9 fine resolution powder diffractometer at the BERII research reactor.

The investigations showed the martensite-austenite phase transition taking place over a broad temperature range depending on the composition and thermal history of the alloy. The starting room temperature neutron diffractogram shows monoclinic phase (martensite) reported in [2]. When heated for first time a phase transition to cubic austenite [3] starts around 300°C and is finishes at 400°C. After further heating to 600°C and adjacent cooling down to room temperature a two-phase mixture was observed (martensite/austenite) showing the thermal memory effect when heated up to 70°C by forming again pure cubic austenite. Obviously the shape memory effect works independently from the phase purity and moreover works just with phase mixtures. The contribution will show all results in detail and give a brief overview into the functioning of shape memory alloy.

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**Keywords: shape memory, phase transition, nitinol**

#### FA2-MS13-P13

**Structural study by X-ray profile analysis and thermodynamics properties of Cu-Cr and Cu-Mo alloys processed by mechanical alloying.** Claudio Aguilar<sup>a</sup>, Paula Roja<sup>b</sup>, Stella Ordoñez<sup>c</sup>, Danny Guzman<sup>d</sup>  
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Technologically, it is interesting to pursue the development of novel high performance materials obtained using a non-equilibrium process, such as mechanical alloying (MA). Today, attention has been concentrated on synthesis of high performance materials such as intermetallics, amorphous metallic alloys and nanocrystalline materials (NCM) [1]

The alloys were synthesized using Cu-5 and 8 wt.% Cr and Cu- 5 and 8 % Mo. The mixtures were placed in a stainless steel container with a 25 ml capacity and milled in a SPEX 8000D mill under an argon atmosphere between 0.5 and 50 h. The alloys were characterized by scanning and transmission electron microscopy- SEM and TEM, x-ray diffraction- XRD, Vickers microhardness- HV and differential scanning calorimetry- DSC. X-ray profile analysis was made using the modified Warren-Averbach and Williamson-Hall methods [2].

The grain size decreased as the milling time increased to values around 10 nm, the dislocation density increased until values of  $1 \times 10^{12} \text{ m}^{-2}$ . Stacking fault energy decreased in the Cu-Cr system until 20 mJ/m<sup>2</sup> and in the Cu-Mo until 10 mJ/m<sup>2</sup> and stacking fault probability increased to  $10^{-2}$  and  $10^{-3}$ , for

both systems respectively. The higher HV values were measured for Cu-Mo alloys for all milling times. The typical values at 50 h of milling were around 280 HV. All alloys presented anisotropic strain, which was better interpreted applying modified Warren-Averbach and Williamson-Hall methods. These results show that anisotropic strain is caused by presence of dislocations in both systems. Due to the disappearance of peaks of Cr and Mo, decrease and increase of lattice parameter of Cu-Cr and Cu-Mo, respectively, and decrease of stacking fault energy, confirm the formation of solid solution in both systems, which are immiscible with a positive enthalpy mixing.

The extension of solid solution was modeled using a regular solution model. The increment of free energy due to the presence of crystalline defects was estimated, for the crystalline defects increasing the free energy, and free curves are moved upwards, hence the solubility limit changes. For Cu-Cr system it was that free energy increase until reach values around 8 kJ/mol and for Cu-Mo system until 10 kJ/mol when milling time increase. These values are higher than the mixing free energy of the solution determined using a regular solution model. These results confirm the formation of solid solution of both systems.

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**Keywords: X-ray diffraction and structure, Thermodynamics, Crystalline defects**

#### FA2-MS13-P15

**The crystal structure of FeAl<sub>2</sub>,** Ihor Chumak<sup>a</sup>, Klaus W. Richter<sup>b</sup>, Helmut Ehrenberg<sup>a</sup>. <sup>a</sup>Institute for Complex Materials, IFW Dresden, Germany. <sup>b</sup>Department of Inorganic Chemistry/Materials Chemistry, University of Vienna, Austria.  
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The crystal structure of FeAl<sub>2</sub> was described first by Corby and Black [1]. The authors solved the structure by use of the anomalous dispersion technique in a trigonal model with 18 atoms per unit cell: space group *P1* (№ 1), Pearson symbol *aP18*,  $a = 4.878(1) \text{ \AA}$ ,  $b = 6.461(2) \text{ \AA}$ ,  $c = 8.800(3) \text{ \AA}$ ,  $\alpha = 91.75(5)^\circ$ ,  $\beta = 73.27(5)^\circ$ ,  $\gamma = 96.89(3)^\circ$ . Our X-ray single crystal investigations confirm the trigonal structure ( $a = 4.875(1) \text{ \AA}$ ,  $b = 6.455(1) \text{ \AA}$ ,  $c = 8.736(1) \text{ \AA}$ ,  $\alpha = 87.93(1)^\circ$ ,  $\beta = 74.40(1)^\circ$ ,  $\gamma = 83.06(1)^\circ$ ), but with one additional atom per unit cell (Pearson symbol *aP19*) and space group *P-1* (№ 2). The FeAl<sub>2</sub> structure derives from the orthorhombic YPd<sub>2</sub>Si structure (ordered Fe<sub>3</sub>C type, space group *Pnma* (№ 62), Pearson symbol *oP16*,  $a = 7.303(2) \text{ \AA}$ ,  $b = 6.918(2) \text{ \AA}$ ,  $c = 5.489(1) \text{ \AA}$ ) [2] by including of 3 additional atoms per unit cell and strong deformation. Both structures can be represented as an arrangement of the trigonal prisms, with noticeable distortions in the case of FeAl<sub>2</sub>.

[1] Corby R. N., Black P.J., *Acta Cryst.*, 1973, B29, 2669. [2] Moreau J.M., le Roy J., Paccard D., *Acta Cryst.*, 1982, B38, 2446.

**Keywords: X-ray structure determination, aluminium alloys, crystal chemistry of alloys.**