SNBL	**Experiment title:** Determination of complex crystal structures of ternary intermetallic compounds in Mo-{Pt,Ru}-Si alloys systems by high resolution and resonant X-ray diffraction	**Experiment number**: 01-01-765
Beamline: BM01B	**Date of experiment**: from: 16-May-08 to: 20-May-08	**Date of report**: 25-Feb-09
Shifts: 12	**Local contact(s)**: Hermann EMERICH	*Received:*

Names and affiliations of applicants (* indicates experimentalists):

Radovan Černý[1]
*Yaroslav Tokaychuk[2]
*Jean-Marc Joubert[2]

[1]Laboratoire de Cristallographie, Université de Genève, 24, quai Ernest-Ansermet CH-1211 Genève 4, Switzerland
[2]Institut de Chimie et des Matériaux Paris-Est, 2-8 rue Henri Dunant, F-94320 Thiais, France

Background

Efforts to improve $MoSi_2$-based refractory material performances lead to the investigation of the ternary systems Mo-{Pt,Ru}-Si and determination of the crystal structures of new ternary intermetallic compounds. This present work is carried out in the frame of the MITECT project (Modelling Intermetallics using Theory, Experiments and Computational Thermodynamics) funded by the Agence Nationale de la Recherche, which is dedicated to the multiscale fundamental study of ternary refractory systems involving the investigation of phase equilibria, determination of the crystal structures of new ternary phases, *ab initio* calculations of phase properties and modelling of individual phases using the CALPHAD method.

Mo-Pt-Si. Three new ternary compounds were found to exist in the Mo-Pt-Si system at different temperatures. The crystal structure of one of them, the Z phase $Mo_3Pt_2Si_2$, remains unknown. Laboratory X-ray powder diffraction had revealed a very complex crystal structure necessitating high resolution synchrotron powder diffraction for the indexation and *ab initio* determination.

Mo-Ru-Si. The isothermal section of Mo-Ru-Si phase diagram at 1673 K was published in [1] and was corrected in [2]. Six ternary phases were found at the temperature of investigation – so called α, β, γ, δ, ε and κ. The crystal structure of three of them, δ (~$Mo_{15}Ru_{50}Si_{35}$), ε (~$Mo_{17}Ru_{58}Si_{25}$) and κ (~$Mo_{10}Ru_{55}Si_{35}$) remains unknown. Non-stoichiometry and large homogeneity domains characterize those phases. High resolution synchrotron powder diffraction data are essential for the indexation and *ab initio* determination of the crystal structures. Moreover, the determination of Mo (Z=42) and Ru (Z=44) distribution over the available atomic sites is only possible by using more than one diffraction data set with different diffraction contrasts between Mo and Ru. In this case, the use of resonant powder diffraction is a solution to enhance the diffraction contrast.

Experimental

Conventional capillary (0.3 mm) Debye-Scherrer technique has been used. One high-resolution pattern for Z-Mo-Pt-Si sample have been measured at $\lambda \sim 0.4$ Å (~30 keV). High energy was required by the high absorption of the samples (μ (@ 30 keV) = 260 cm^{-1}). Two powder diffraction data sets have been measured for each Mo-Ru-Si sample: one far above the Mo absorption K-edge (~30 keV), and the other 10 eV before the Mo K-edge (~20 keV). This allowed us to obtain diffraction data sets with different diffraction contrast between Mo and Ru due to the resonant contribution of Mo (f' = -7 e^-). The exact position of the Mo K-edge has been calibrated by a XANES scan of the compound and various Si diffraction scans.

Results

Mo-Pt-Si

The structure of the Z phase has been entirely solved from the collected data. Indexation was made using TOPAS (*Cc*, *a*=13.887 Å, *b*=8.077 Å, *c*=9.611 Å, β=100.90°) and structure solution using FOX (17 independent atoms). The final refinement of the crystal structure was made with FULLPROF. The analysis of the crystal structure reveals coordination polyhedra very close to Frank-Kasper coordination, in contrast with the two other ternary phases of the systems which are typical silicides deriving from PtSi (X-$MoPt_2Si_3$ and Y-$MoPt_3Si_4$). This makes appear a change of the nature of bonding in the system with the composition: covalent bonding in the silicon rich region (X and Y phases, PtSi), strictly metallic bonding in the Mo and Pt rich region (*Z* phase, *A*15 Mo_3Pt and Mo_3Si).

Mo-Ru-Si

Additional peaks were found in the resonant data of the ε phase as regards the structural model established on conventional diffraction data. This indicates a complex Mo/Ru ordering not detectable in the absence of resonant phenomenon. The complete indexing is underway.

For the δ phase, the same behaviour could be evidenced. We succeeded in indexing the superstructure of the TiCu type evidenced on laboratory data by tripling both lattice parameter. The complete refinement of the site occupancy data is underway.

The κ phase has a crystal structure very close to the δ phase. However, the type of ordering could not yet be evidenced with certainty. Again, we are working on the determination of the correct cell.

When this has been done, we will refine the whole structures using both data sets.

[1] A. Littner, M. Francois, B. Malaman, J. Steinmetz, M. Vilasi, E. Elkaim, "Isothermal section at 1673 K of the Mo-Ru-Si diagram and crystallographic structures of ternary phases", *Intermetallics*, **11** (2003) 1223-1228.

[2] A. Littner, Thèse de Doctorat, Université de Nancy Henri-Poincaré (2006).