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|---|---|---|
| **Beamline**: ID31 | **Date of experiment**: from: 22/09/04 to: 25/09/04 | **Date of report**: 06/02/06 |
| **Shifts:** 9 | **Local contact(s)**: Andy FITCH | *Received at ESRF:* |


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## Report:

In spite of a very promising potential for a large field of high temperature applications, $MoSi_2$ shows only a limited resistance against molten glass corrosion. Efforts to improve $MoSi_2$-based material performance led to the development of new structural materials through additions of Ru. A good knowledge of the ternary system was required in order to specify alloy compositions, synthesis conditions, limiting conditions of uses. Therefore, investigations of the isothermal section at 1400°C of the Mo-Ru-Si system X-ray diffraction, SEM (Scanning Electron Microscopy) and EPMA (Electron Probe Micro Analysis) has been carried out.

The crystallographic structures of the new silicides have been characterized using synchrotron powder X-ray diffraction at line ID31 at ESRF. Distribution of Mo (Z=42) and Ru (Z=44) is evidenced by anomal X-ray diffraction at the Mo threshold and multipatterns refinement with Rietveld method using Fullprof_suite software. Here we report most the significant results concerning the phases α, β and γ. This work was presented in [1].

### phase α:

For the phase α which have the cubic FeSi structure-type (P $2_13$ ; a =4.75640(2) Å), a three pattern refinement have been performed. The refinement parameters, including the f' and f'' value used for each wave length are reported in Table I. The refinements lead to very satisfactory R factors. An example of a fit by the Rietveld method is reported in Fig.1. The main result obtained for this simple phase is the X-ray refined composition, which is to be compared to EPMA results. Inter atomic distances are reported in Table II.

Compositions : EPMA: Mo 6.9(2) Ru 42.8(2) Si 50.3(2)
RX-Refined : Mo7.8(1) Ru 42.2(1) Si 50

In conclusion, the method we proposed for the localisation of Mo and Ru in this structure containing only two metallic site lead to very satisfactory results.

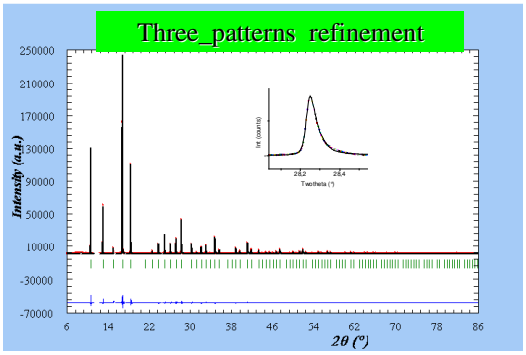


Fig.1 : Refiend X ray diffraction pattern for the phase α

Table II : Inter atomic distances in the phase α

| Site | Site | Distances (Å) |
|---|---|---|
| M1 | 1 M2 | 2.405(1) |
| | 3 M2 | 2.460(1) |
| | 3 M2 | 2.699(1) |
| | 6 M2 | 2.950(1) |
| M2 | 4 M1 | 2.405(1) |
| | 3 M1 | 2.460(1) |
| | 6 M1 | 2.914(1) |

**Table I:** Parameters of the three patterns refinement

| Wave length (Å) | F' | F'' |
|---|---|---|
| 0.620247 | Mo: -6.4640 | 0.539 |
| | Ru: -1.92300 | 0.651 |
| 0.619852 | Mo: -8.9970 | 3.697 |
| | Ru: -1.92300 | 0.651 |
| 0.632460 | Mo: -3.2750 | 0.559 |
| | Ru: -1.78000 | 0.674 |

| Alpha phase | FeSi type |
|---|---|
| x(M1) | 0.84045(15) |
| x(M2) | 0.13235(7) |
| Occupancy | M1: 100 % Si |
| | M2: 15.6 (0.14) % Mo |
| | 84.4 (0.14) % Ru |
| Function used | Split PV |
| $R_p$: % | 6.1, 6.0, 6.0 |
| $R_{wp}$: % | 9.40, 9.3, 9.4 |
| $R_{exp}$: % | 2.7, 3.3, 3.3 |
| $R_B$: % | 2.6, 3.8, 3.2 |
| $R_F$: % | 1.9, 3.4, 2.6 |

## Phase β :

The nominal composition of the β phase is $Mo_{26}Ru_{47}Si_{27}$. Its structure was determined previously (LURE data) by Ab-initio method. P 4/mmm a =9.216(1)Å c=2.887(1) Å [1]. A two pattern refinement has been performed (see Fig. 2). Due to the fact that the sample appears heterogeneous when inspecting the reflection profile (shoulders in the profiles), two phases β supposed to have very near parameters and composition have to be included in the refinement model as reported in the Table III.

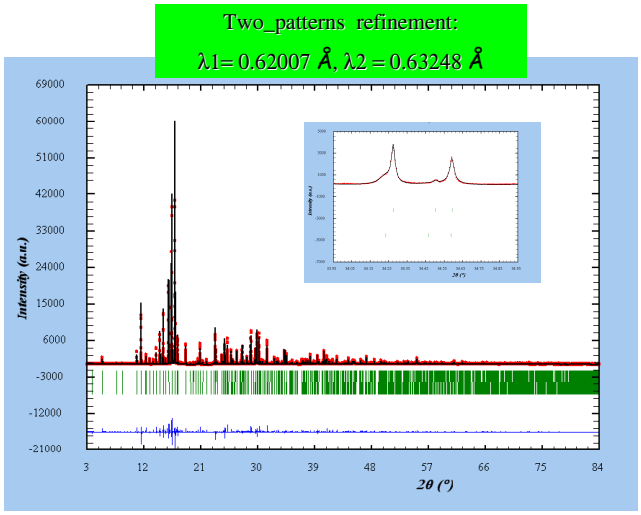


Fig.2 : Refinement of X ray diffraction pattern for the phase β including two phases.

Table III : Refined atomic parameters for the β phase.

| Site | B(Å$^2$) | Phase 1 | Phase 2 |
|---|---|---|---|
| Lattice (Å) | | A = 9.22182 | A = 9.22011 |
| | | C = 2.88695 | C = 2.89368 |
| RF % | | 7.7/10.4 | 9.0/11.0 |
| M1 (4n) [y = 0.21191(10)] | 0.232(13) | 4 Ru | 4 Ru |
| M2 (4j) [x = 0.15718(7)] | 0.190(13) | 4 Ru | 4 Ru |
| M3 (1d) | 0.729(44) | 1 Ru | 0.7(1) Mo/ 0.3(1) Ru |
| M4 (4m) [x = 0.36152(12)] | 0.729(-) | 4 Mo | 4 Mo |
| Si1 (1b) | 0.426(106) | 1 Si | 1 Si |
| Si2 (4k) [x = 0.30245(28) | 0.604(60) | 4 Si | 4 Si |
| Refined composition | | Mo4Ru9Si5 | Mo4.7(1)Ru8.3(1)Si5 |

Despite the heterogeneity of the sample, which could not be seen from X-ray laboratory, localization of Ru and Mo atoms could be obtained. Localization of the Mo atoms in the M3(1d) site expected from DFT calculation using KKR method is verified [2].

Table IV : Selected interatomic distances in the phase β

| Site | Sites | d(Å) | site | site | d(Å) |
|---|---|---|---|---|---|
| M1 | 4 M4 | 2.515(1) | M4 | M1 | 2.515(1) |
| | 4 M2 | 2.752(1) | | M4 | 2.588(2) |
| | 4 M5 | 2.812(1) | | 2 M3 | 2.696(2) |
| | | | | 2 M3 | 2.701(1) |
| M2 | 2 M3 | 2.617(1) | | 2 M5 | 2.739(2) |
| | M2 | 2.684(1) | | 2 M5 | 2.745(2) |
| | 2 M1 | 2.812(1) | | 2 M5 | 2.739(2) |
| | 4 M4 | 2.906(1) | | | |
| | 4 M5 | 3.059(1) | M5 | M5 | 2.463(2) |
| | 2 M5 | 3.145(1) | | M5 | 2.480(2) |
| | | | | 2 M4 | 2.739(1) |
| M3 | M3 | 2.562(1) | | 2 M4 | 2.745(1) |
| | M2 | 2.617(1) | | M1 | 2.752(2) |
| | 2 M4 | 2.696(2) | | 2 M3 | 2.977(1) |
| | 2 M4 | 2.701(1) | | 2 M3 | 2.980(1) |
| | 2 M5 | 2.977(1) | | 2 M2 | 3.059(1) |
| | 2 M5 | 2.980(1) | | M2 | 3.145(1) |
| | 4 M3 | 3.064(1) | | | |

**Phase γ**

The structure of the phase γ (nominal composition $Mo_{10}Ru_{40}Si_{50}$) has been solved from the present synchrotron powder diffraction data by ab_initio methods using the software EXPO [2]. It crystallizes in the cubic space group I -4 3 m wit lattice parameter a =9.36429(1)Å. A single pattern (λ = 0,63248(2) Å) have been used for the refinement of the structure (see Fig. 3). The structure contains four metallic sites as seen on Fig.4. As the previous sample, heterogeneity well seen from these high resolution data have been taken into account in the refinement process. It was clear that the sample contains two phases β with close lattice parameters and composition. The refined parameters are reported in the Table V.

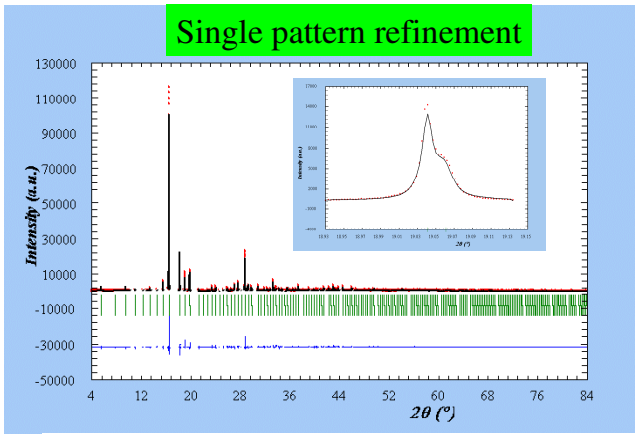


Fig.3 : Rietveld refinement for γ phase.

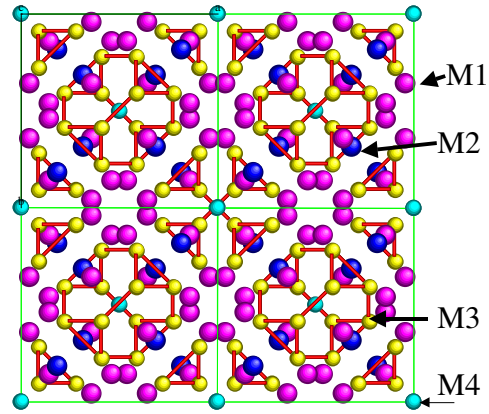


Fig.4 : structure of the phase γ

Table V : : Refined atomic parameters for the phase γ.

| Site | Phase 1<br>a=9.36665(2) | Phase 2<br>a= 9.35703(5) |
|---|---|---|
| RF % | 8.8 | 12.9 |
| M1 (24g) x=0.3578(1), z = 0.0408(1) | 19.6(1) Ru / 4.3 (1) Mo | 24 Ru |
| M2 (8c) x = 0.3157(2) | 8 Ru | 8 Si |
| M3 (24g) x = 0.4105(2), z = 0.2209(3) | 16.3 (1) Mo/ 7.7 (1) Si | 18.7(1) Mo/ 5.3 (1) Si |
| M4 (2a) | 0.7 Mo / 1.3 Ru | 2 Mo |
| Composition (EPMA = 41/41/18) | Mo37Ru50Si13 | Mo36Ru41Si23 |

Table V : : Inter atomic distances in the phase γ.

| Atom | Atom | Distances(Å) | Atom | Atom | Distances |
|---|---|---|---|---|---|
| M1 | 1 M3 | 2.548(3) | M3 | 1 M3 | 2.370(3) |
| | 1 M2 | 2.635(2) | | 2 M3 | 2.512(3) |
| | 2 M3 | 2.660(2) | | 1 M1 | 2.548(3) |
| | 2 M1 | 2.768(1) | | 2 M1 | 2.660(2) |
| | 2 M3 | 2.790(2) | | 2 M1 | 2.790(2) |
| | 4 M1 | 2.815(2) | | 2 M2 | 2.855(2) |
| | | | | 1 M4 | 2.870(2) |
| M2 | 3 M1 | 2.635(2) | | 2 M2 | 3.018(3) |
| | 6 M3 | 2.854(2) | | | |
| | 1 M4 | 2.988((2) | M4 | 12 M3 | 2.871(2) |
| | 3 M3 | 3.018(3) | | 4 M2 | 2.988(2) |

## Conclusion:

The aim of the experiments realized in the ID31 beam line of ESRF led to very conclusive results. Firstly we have for the phase α (two metallic sites) a good agreement between the composition determined from EPMA and the powder ID31 diffraction data. Secondly, the objective of localization of the Mo and Ru atoms in a more complex structure (Five metallic sites) has been reach. Thirdly, the structure of the phase γ (four metallic sites) have been solved by ab-initio method. The only problem we encountered is that the sample appears heterogeneous with such high resolution data and increase the complexity of the Rietveld refinements.

**References:**

[1] M. François, M. Vilasi, E. Elkaim, F. Zamoun, 'Structures in Mo-Ru-Si by Powder and Anomal X-ray Diffraction', Acta C (2005), A61, C158, XX Congress of the International Union of Crystallography, Florence, 23-31 August 2005

[2] A. Littner, M. François, J. Tobola, E. Elkaim, B. Malaman, M. Vilasi : « Ab-initio crystal structure of Mo4+xRu9-xSi5 ($0 \leq x \leq 1$) by synchrotron powder diffraction and electronic properties calculation (KKR method) Intermetallics 13 (2005) 1048-1055

[3] Altomare A., Burla M.C., Cascarano G. L., Giacovazzo C., Guagliardi A., Moliterni A.G.G., Polidori G, Rizzi R., Camalli M., J. Appl. Cryst 32 (1999) 339.