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Direct Synthesis of TiCr₂ Powder by Calciothermic Co-reduction of their Oxides in Molten CaCl₂

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Abstract

A new process is studied to synthesize an intermetallic compound TiCr₂ directly from the oxide mixture of Cr₂O₃ and TiO₂. This method combines the calciothermic co-reduction and the *in situ* dissolution of the by-product CaO into the molten salt. The molten CaCl₂ was needed to dissolve CaO for complete reaction, and the reduction and alloying occurred simultaneously and quickly in this media. Because of the narrow compositional range of TiCr₂, however, a small amount of Ti and Cr coexisted with α -TiCr₂. The high temperature form, β -TiCr₂, was not found probably because it decomposed into α -TiCr₂ and Cr during cooling. The obtained alloy powder showed capability of hydrogen storage after activation.

Keywords: co-reduction, molten salt, hydrogen storage alloy, inorganic synthesis

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1. Introduction

Intermetallic compound TiCr₂ can absorb hydrogen at room temperature when high pressure of hydrogen gas is applied^{1,2)}. To improve its surface sensitivity, pulverization and the operating conditions for hydrogen absorption and adsorption, the Ti-Cr-V based alloys have been developed³⁻⁸⁾, and it is nominated as one of the promising hydrogen storage alloys.

In the industrial production of the elemental metals of these alloys, the most stable V and Ti oxides are once converted to the chlorides and reduced by Mg in batch-type operation, and Cr is extracted by the electrolysis or reduced by Al or Si. These metals are then arc-melted several times for alloying, heated for homogenization, pulverized and finally activated for hydridation. These long thermal processes from the oxides to the desired alloy powder waste a large amount of heat and electricity, and it may become a barrier for mass production of these alloys.

This work is planned to simplify the synthesizing process aiming at energy saving.

Fig.1 illustrates our proposal that the oxide mixture is simultaneously reduced and converted to the alloy powder. The co-reduction using calcium was reported as a successful method to synthesize the solid solution such as Ti-Al and Nb-Al binary alloys⁹⁻¹³⁾ or intermetallic compounds such as TiAl, SmCo₅ and Nb₃Sn¹³⁻¹⁵⁾.

The purpose of this work is to apply the co-reduction technique to form the binary compound TiCr₂ as the hydrogen storage material, and to confirm experimentally this feasibility for further application to the ternary or quaternary alloys.

The basic mechanism of calciothermic co-reduction was reported in detail previously¹⁶⁾ and only a brief outline will be described here.

Thermodynamically it is the most difficult to reduce Ti mono-oxide (TiO) among Ti and Cr oxides, because the oxygen potential in the equilibrium of Ti/TiO is the lowest, as shown in Fig.2^{17,18)}. Due to the low potential of Ca/CaO, calcium can reduce both the Ti and Cr oxides to the metallic state, and it does not make an alloy with these metals. We expect a simultaneous alloying during the reduction process.

Previous attempts of calciothermic co-reduction, however, showed that the by-product CaO of this reduction disturbs the reduction and alloying^{9-12,15,16)}. Okabe *et al.* proved in the deoxidation of pure Ti that the molten CaCl₂ was effective to remove CaO^{19,20)}, because CaCl₂ could dissolve about 20 mol% CaO at 1173 K²¹⁻²³⁾. It was also reported in the reduction of the pure oxides such as TiO₂²⁴⁻²⁶⁾, Ta₂O₅^{27,28)} and Nb₂O₅^{29,30)}. The by-product CaO could be eliminated *in-situ* into the molten CaCl₂ and the Ca reduction and deoxidation was enhanced. For the oxide mixture, we expect that all of the chemical reactions, i.e., reduction, deoxidation and alloying, would be accelerated

by the addition of CaCl₂, as shown in Fig.3. The alloying between the two metals, M_1 and M_2 , will be enhanced by the CaO removal into the molten CaCl₂, although Ca liquid flows above the molten CaCl₂. It is noted that Ca can dissolve in a few mol% in the CaCl₂³¹⁻³⁴⁾ as the effective reductant, and that CaCl₂ is thermochemically stable even in such a strong reducing atmosphere¹⁷⁾.

The previous studies succeeded to synthesize Nb-Ti and V-Ti solid solutions using calciothermic co-reduction in CaCl₂^{16,30)}. Therefore, the addition of CaCl₂ would be effective to synthesis the intermetallic compounds such as the hydrogen storage TiCr₂. The purpose of this work is to synthesize TiCr₂ in the molten CaCl₂ from the oxide mixture.

2. Experimentals

2.1 Materials

This work used TiO₂ (rutile type) and Cr₂O₃ powders with high purity (>99%) and sub micron size. Ca lumps (>99%) and granular CaCl₂ anhydrate (99.0%) were used as the reductant and the molten media, respectively. About 10g of the oxides were well mixed in the mortar at the desired atomic ratio of Ti and Cr. The possible routes such as sol-gel method or co-precipitation method for oxide mixing were not taken to test the practical applicability.

2.2 Apparatus for co-reduction

Fig.4 illustrates the apparatus for the co-reduction. Based on the previous report¹⁶⁾, the oxide mixture and Ca was embedded together with CaCl₂ (about 300 g in maximum) at the bottom part of stainless steel vessel (93 mm in I.D., and 78 mm in depth). The molar ratio of Ca and CaCl₂ was set constant throughout this study to be Ca:CaCl₂=7:93²⁶⁾. When the reaction is completed under this mixing ratio, there will remain a small amount of Ca liquid and the concentration of CaO in CaCl₂ will be kept in a few mol%. The vessel was locked to minimize the possible leakage of Ca vapor. It was set in the furnace, evacuated and heated upto 773 K for dehydration. It was successively heated in a purified Ar gas atmosphere upto 1073K or 1173 K. After the desired time, it was cooled in the furnace. The sample was rinsed with the distilled water to remove the solidified salt. Subsequently it was washed in acetic acid, water and ethanol for several times, filtered or centrifugally separated, and dried in vacuum.

2.3 Analysis

The phases in the recovered samples were identified by X-ray diffraction measurement (XRD) using ICDD-JCPDS database. The oxygen and hydrogen concentration was analyzed by an inert gas fusion – infrared absorption method using

LECO TC-336 and by a high frequency melting – infrared absorption method using LECO RH-402, respectively. The powder morphology was examined by scanning electron microscopy (SEM) including data obtained with an energy dispersive X-ray analyzer (EDX). Its accuracy for Ti concentration was 0.8 and 0.2 mol%Ti in the case of powder and bulk form, respectively. The hydrogen storage property was measured by the Sievelts method^{1,2,35)} at 243 K using the methanol bath.

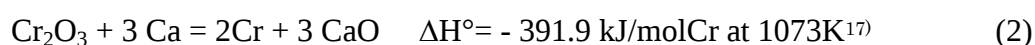
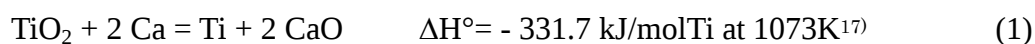
3. Results and Discussions

3.1 Calciothermic co-reduction without CaCl₂

TiCr₂ has a narrow non-stoichiometry³⁶⁾, and the crystalline data as its single phase was reported at the molar ratio of Ti:Cr=1:1.84³⁷⁾. The starting oxide mixture (Ti:Cr=1:1.84 in molar ratio) was firstly mixed only with the metallic Ca lumps, without CaCl₂. The amount of Ca was twice the stoichiometric amount for reduction, considering the leakage of Ca vapor. They were heated at 1073 K for 7.2 ks in Ar gas atmosphere. After the reaction, a trace of partial melting and a significant exothermic reaction with splash were found in the vessel, because some parts of the sample were scattered on the vessel wall and the raw material Cr₂O₃ was found there. After removal of the residual Ca and CaO from the sample at the bottom of crucible using the aqueous solutions, the obtained gray powder was identified as a complex mixture of Cr-O, TiO,

CaTiO₃, TiO_{0.323} and Cr, as shown in Fig.5, although the formation of the single phase of TiCr₂ was expected.

The fundamental reactions in the vessel are as follows, if we neglect the formation of the intermediate phases such as CaTiO₃,



These significant and sudden exothermic reactions heat the oxide mixture locally, and enhance the alloying between the reduction products of Ti and Cr, while it evaporates the reductant Ca. The small leakage of Ca vapor from the reaction vessel is one of the reasons why the reduction does not complete and the by-product CaO reacts with the residual TiO₂ to form CaTiO₃. Another strong reason is a sudden splash of the sample powder due to local exothermal reaction.

3.2 Calciothermic co-reduction with CaCl₂

A homogeneous solvent such as the molten CaCl₂ is effective to suppress the excessive chemical reaction accelerated by the local exothermic heat. Hereafter, we report only the results when CaCl₂ was used. The filling method as shown in Fig. 4 was taken because it was reported as the most effective way for the reduction^{16,27,28)}. The oxides located closely with calcium lumps in the CaCl₂ powder, but do not contact

directly. After melting of CaCl₂, the excess amount of Ca flows upward above the CaCl₂ melt (about 20 mm in depth). After the experiments, it was commonly observed that a small amount of Ca solidified on the CaCl₂ along the vessel wall, in addition to evaporation of Ca and its precipitation on the inner surface of the lid.

3.3 Oxygen concentration

The oxygen removal from the oxides completed in an early stage of reaction, as shown in Fig. 6. Note that the initial oxygen concentration in the oxide mixture corresponds to 34.5 mass%. The oxygen contents were kept nearly constant after the first one hour. Although the thermodynamic equilibrium oxygen content under Ca/CaO equilibrium is evaluated as about 500 mass ppmO in Ti¹⁸⁾ and <1 ppmO in Cr, it was experimentally reported that 1420 ppmO remained in the Ti powder when pure TiO₂ was reduced in CaCl₂ by Ca at the best condition²⁶⁾. It was also reported that the oxygen contents were 0.543%O and 1.18% when the mixture of V₂O₃ and TiO₂ and that of V₂O₅ and TiO₂ were reduced, respectively¹⁶⁾. It is expected that the oxygen content in this work can be decreased by finding the optimum condition of the mixing ratios of the oxide mixture, Ca and CaCl₂.

3.4 Synthesized phases

Fig. 7 shows the XRD patterns from the samples reacted at 1073 and 1173 K. All the samples contained commonly α -TiCr₂ as the dominant phase, and the small amounts of α -Ti and Cr. The XRD intensities from α -Ti and Cr phases were nearly same even if the time was prolonged or the reaction temperature was varied. No intermitting phase during the reduction such as CaTiO₃ or TiO was found even in a short reaction time. This shows that the co-reduction occurred for the oxide mixture. These findings agreed with the analyzed oxygen contents.

In the Ti-V system, it was reported that the reduction of TiO₂ was delayed due to the melting of starting V₂O₅¹⁶⁾ and due to the preferential reduction of vanadium oxide. This delay in reduction was not found in this Ti-Cr system, probably because the melting points of our oxides are higher than the reaction temperatures.

Fig. 8 shows the XRD patterns of the samples where the mixing ratio of Ti and Cr was gradually changed. All of them were identified as the mixture of α -TiCr₂, α -Ti and Cr.

According to the binary phase diagram³⁶⁾, the stoichiometric compositions of low temperature form, α -TiCr₂, and of high temperature form, β -TiCr₂, are 64 mol%Cr and 66 mol%Cr, respectively. α - and β -TiCr₂ are stable below 1493 K and above 1073 K,

respectively. Both phases have a narrow off-stoichiometry of ± 1 mol%Cr. The samples at the studied compositions of 66.7mol%Cr, 64.8%Cr and 62.0%Cr, therefore, should consist of Cr+ β -TiCr₂, β -TiCr₂ + α -TiCr₂, and α -TiCr₂ + β -Ti, respectively, in equilibrium at 1073 K. The high temperature phases, β -TiCr₂ and β -Ti, would have decomposed during cooling to α -TiCr₂ + Cr and β -Ti, respectively, if β -TiCr₂ and β -Ti were formed at the reaction temperature. Even if this phase transformation occurred in our samples, however, the coexistence of three phases, α -TiCr₂, α -Ti and Cr, can not be explained by the equilibrium phases: the coexistence of α -Ti and Cr is not allowed by the equilibrium phase diagram.

Fig.9 shows the SEM image and its EDX mapping of the powder of 66.7 mol%Cr. The gains were finely dispersed. The averaged concentration by EDX agreed with the target concentration, and most of particles were consistent with the composition of α -TiCr₂. However, some large particles were analyzed as pure Ti or pure Cr. The concentration of some other fine particles were analyzed as a few mol%Ti-Cr (solubility limit in Cr) and as Ti-12mol%Cr (eutectoid composition), which indicates the diffusion after the co-reduction was insufficient or the decomposition product from β -TiCr₂.

3.5 Confirmed mechanism

Fig. 10 illustrates the mechanism of phase formation during the co-reduction from the

mixture of Cr₂O₃ and TiO₂ and the successive cooling, based on the above mentioned experimental evidences. By the *in-situ* removal of CaO into CaCl₂, the reduced β -Ti (or α -Ti-O solid solution, if the deoxidation of Ti was not enough to transform to β -Ti) and Cr react and form the two intermetallic compounds, α -TiCr₂ and β -TiCr₂, by the mutual diffusion aiming at the desired composition. However, the local heterogeneity in the starting oxide mixture causes Ti-rich and Cr-rich regions in the sample, which forms the coexistence of β -Ti and Cr particles in the same sample. They are isolated by the molten CaCl₂ and it rarely reacts together. The decomposition of β -TiCr₂ during cooling precipitates the Cr particles inside the α -TiCr₂. It seldom becomes homogeneous by reacting the isolated Ti particles and the precipitated Cr particles. The coarsening and aggregation of the particles would have promoted the diffusion and alloying if the reaction time could become long enough.

As additional evidence, the sample shown both in Fig. 8 and 9 was successively held at 873 K for 7.2 ks in the solidified salt after the reaction. The amounts of undesired phases after cooling were similar with those in the sample without this additional treatment. This shows that the pure Ti particles isolated by the solidified salt did not react with the precipitated Cr. If they adhered to the surface of the transformed α -TiCr₂ particles, the volume fraction of Cr and α -Ti would have decreased.

3.6 Hydrogen Storage Property

The hydrogen storage curves were measured at 243 K for the powder co-reduced at 1073 K for 7.2 ks, for the reduced and annealed powder, and for the powder arc-melted from Ti and Cr, for comparison. After the measurement at 243 K, the hydrogen contents at room temperature were analyzed and the amounts of hydrogen at 243 K were corrected. Assuming that all the powders consisted of the α -TiCr₂ single phase, the absorbed hydrogen (H/M) was evaluated as shown in Fig. 11.

When the powder was freshly exposed to the purified hydrogen gas atmosphere of 3.8 MPa at 243 K (the highest pressure and the lowest temperature of our apparatus), the hydrogen absorption could not be found for all the powders. It is because an oxide or organic layer generally contaminates the sample surface. An activation treatment was applied prior to the measurements of the hydrogen storage curves, which was taken as a standard procedure for hydrogen absorption.

The samples were activated by three cycles that they were subjected to 3.8 MPa H₂ gas at 673 K for 3.6 ks, evacuated at 243 K for a day and then at 673 K for 3.6 ks. The hydrogen absorption was small at 243 K even after this activation, but a trace of plateau was found as shown in Fig. 11.

Although some differences in the isotherm of these samples were observed compared

to Ref. 1 and 2, the PCT curves for the reduced samples agreed quantitatively with that of α -TiCr₂. The behavior of PCT curves for the arc-melted sample could be explained as the mixture of α -TiCr₂ and β -TiCr₂ due to rapid cooling. These data show that the main phase of α -TiCr₂ in the reduced samples hold the hydrogen absorption capability although it coexisted with the impurity phases.

4. Conclusions

We proposed a new method consisting of calciothermic co-reduction and *in situ* separation of CaO. The oxide mixtures were reduced by metallic Ca to form an intermetallic compound TiCr₂ directly. The usage of CaCl₂ for synthesis of α -TiCr₂ was efficient for CaO elimination, and hindered the formation of intermediate phases such as CaTiO₃.

The oxygen content decreased to 0.3mass%, but a single α -TiCr₂ phase could not be obtained at 1073-1173 K within 72 ks. The compositional deviation in the starting oxide mixture and the decomposition of β -TiCr₂ caused the coexistence of a small amount of the isolated Ti and Cr particles. The activated powder showed capability of hydrogen absorption.

Acknowledgements

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Figure Captions

Fig. 1 Proposed process for synthesis of TiCr₂.

Fig. 2 Oxygen potential in Ti-O and Cr-O binary systems^{17,18)}.

Fig. 3 Mechanism of co-reduction and elimination of CaO into the CaCl₂ melt.

Fig. 4 Schematic illustration of the experimental apparatus.

Fig. 5 XRD pattern of the sample reduced without CaCl₂.

Fig. 6 Oxygen concentration in the powder reacted with CaCl₂ at 1073 and 1173 K.

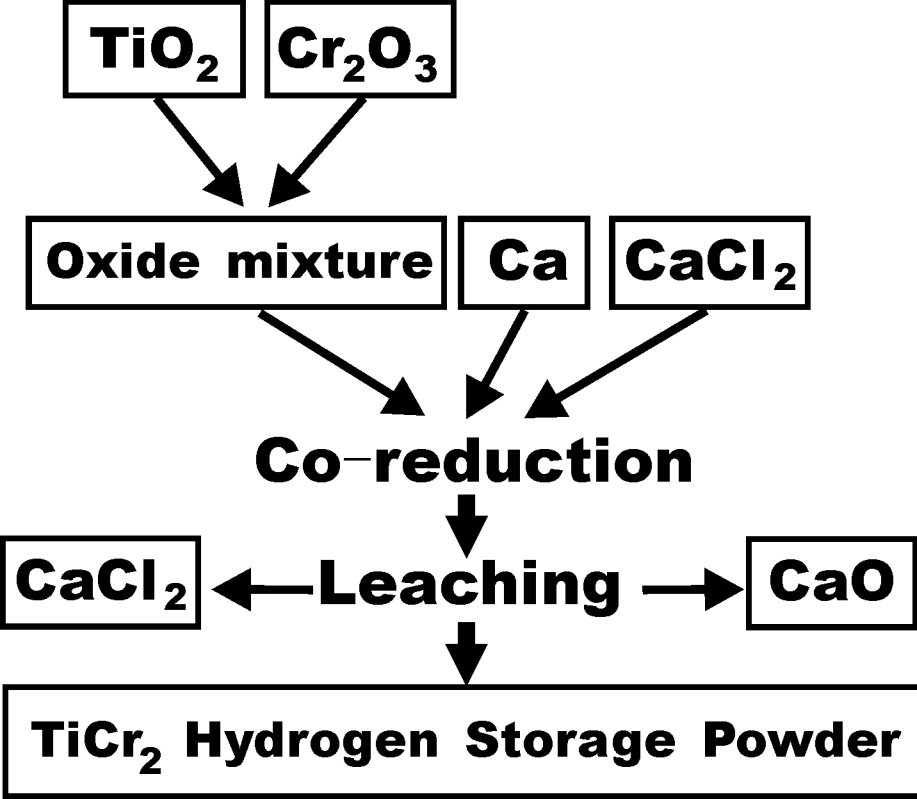
Fig. 7 XRD patterns of the samples reduced with CaCl₂ at 1073 and 1173 K, where the molar ratio of Ti:Cr was 1:2 in the oxide mixture.

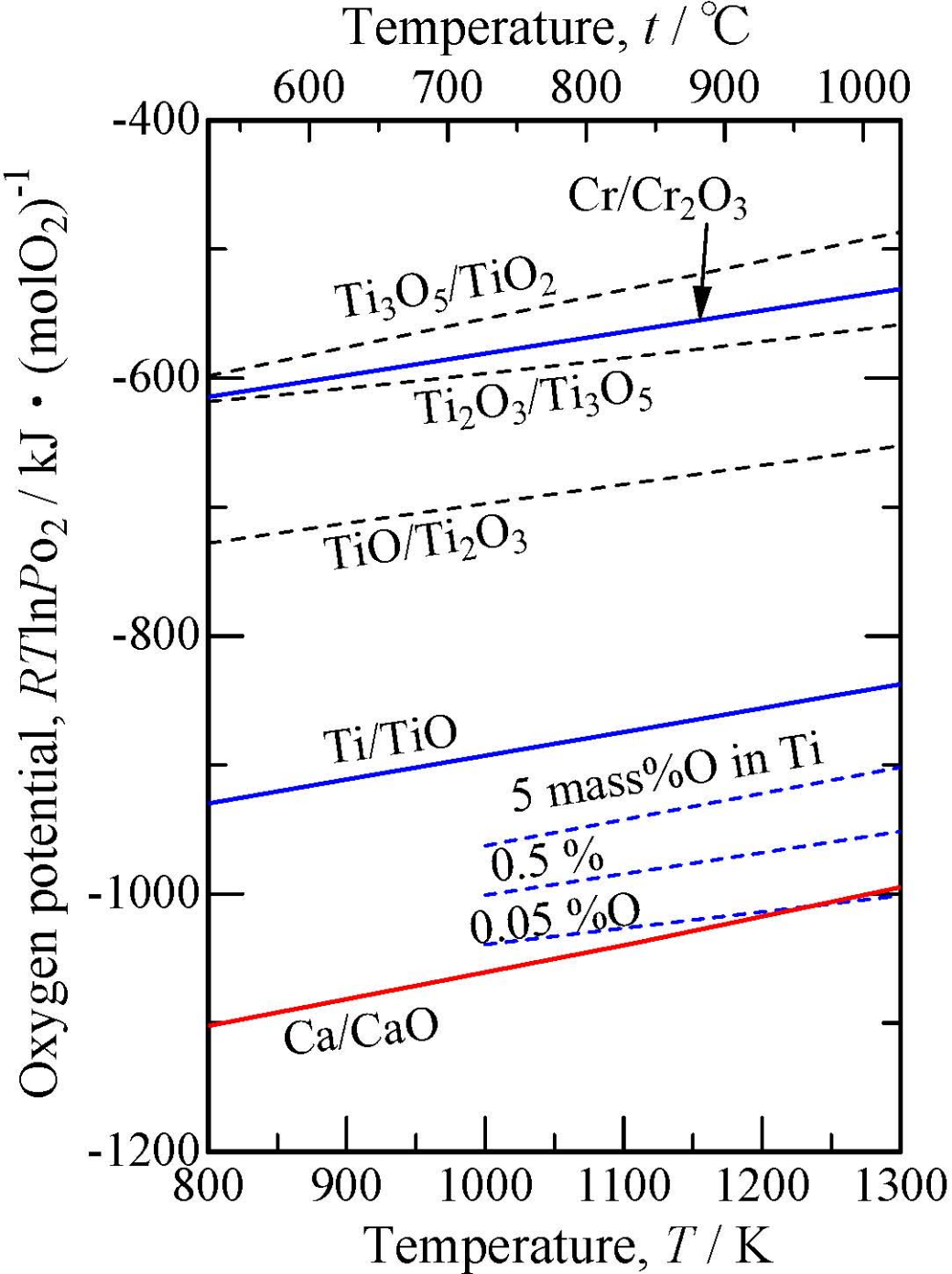
Fig. 8 XRD patterns of the samples reduced with CaCl₂ at 1073 K for 7.2 ks.

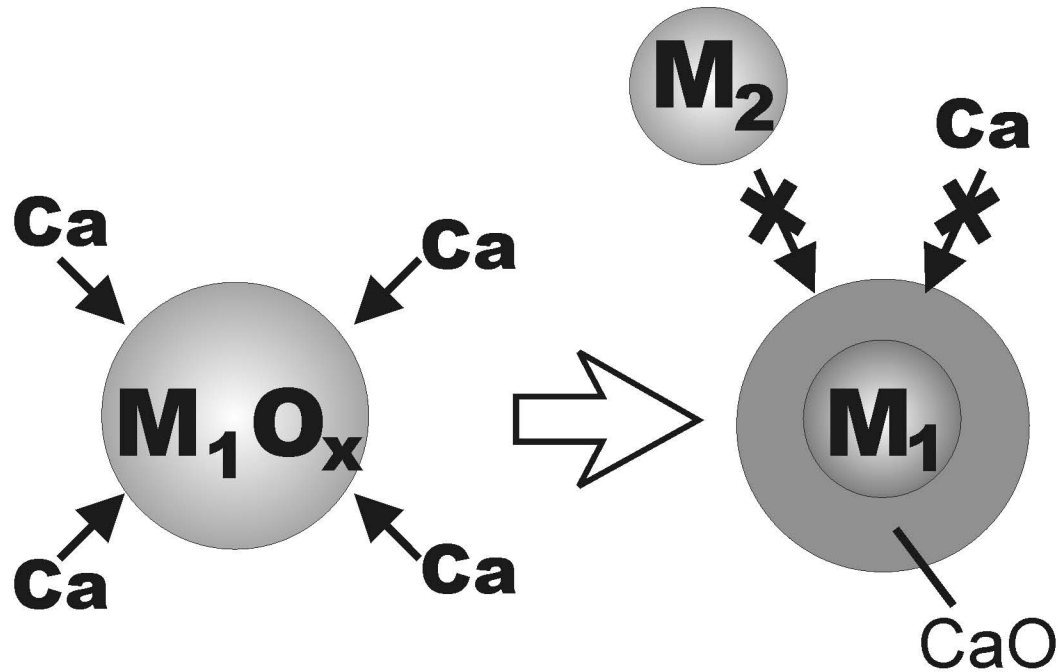
Fig. 9 SEM image and the corresponding elemental mapping of Ti and Cr in the sample reduced at 1073K for 28.8ks.

Fig. 10 Mechanism of phase formation during co-reduction.

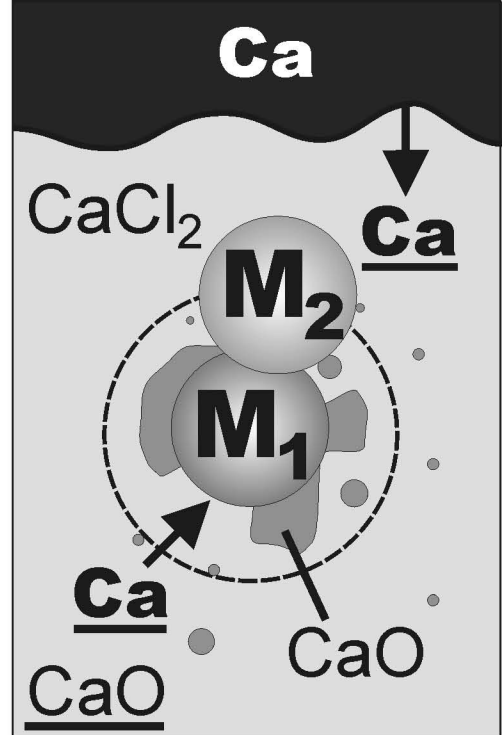
Fig. 11 Pressure-composition isotherms for the sample co-reduced at 1173 K for 7.2 ks and for the sample successively annealed at 873 K for 7.2 ks.



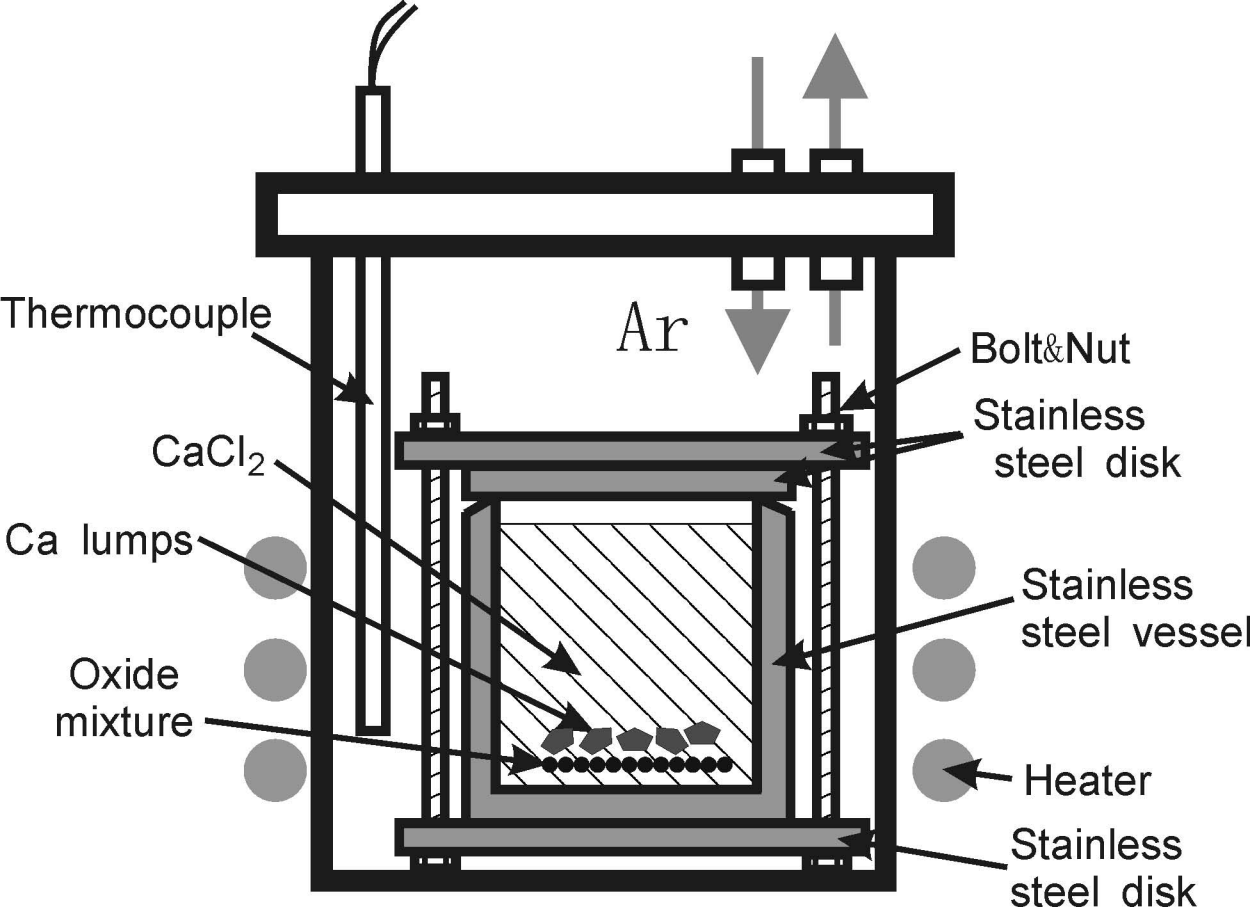


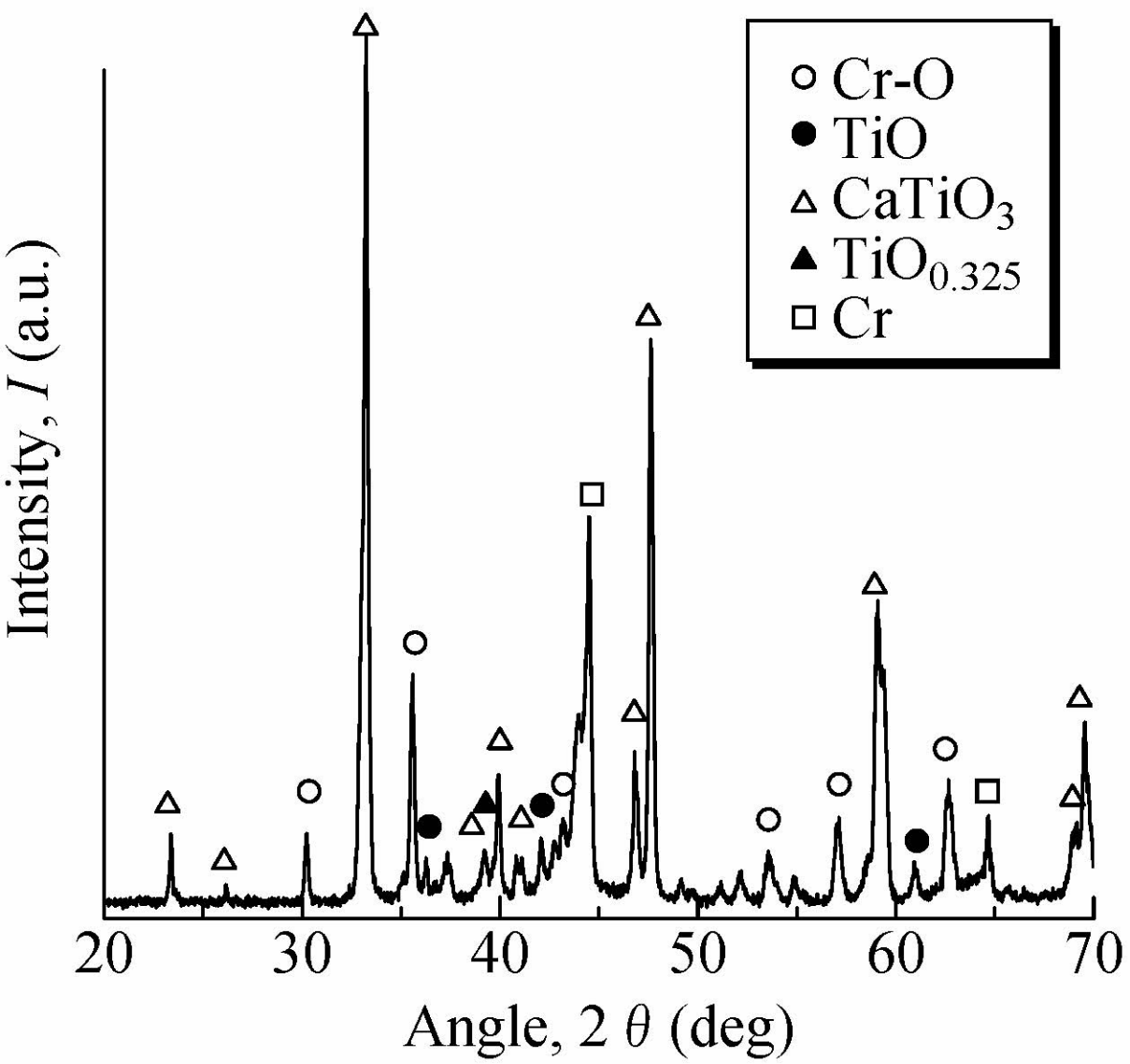


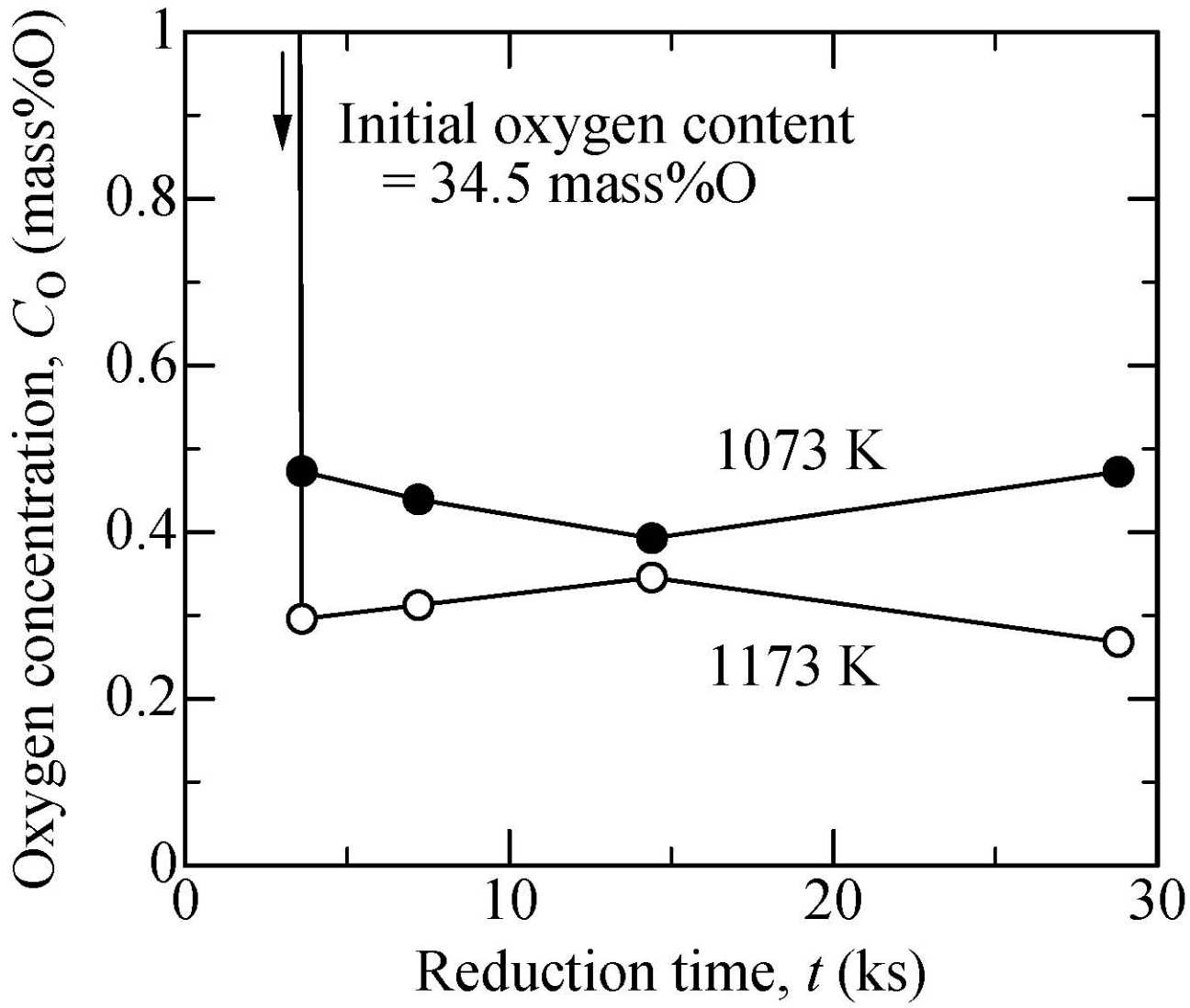
Calciothermic Reduction

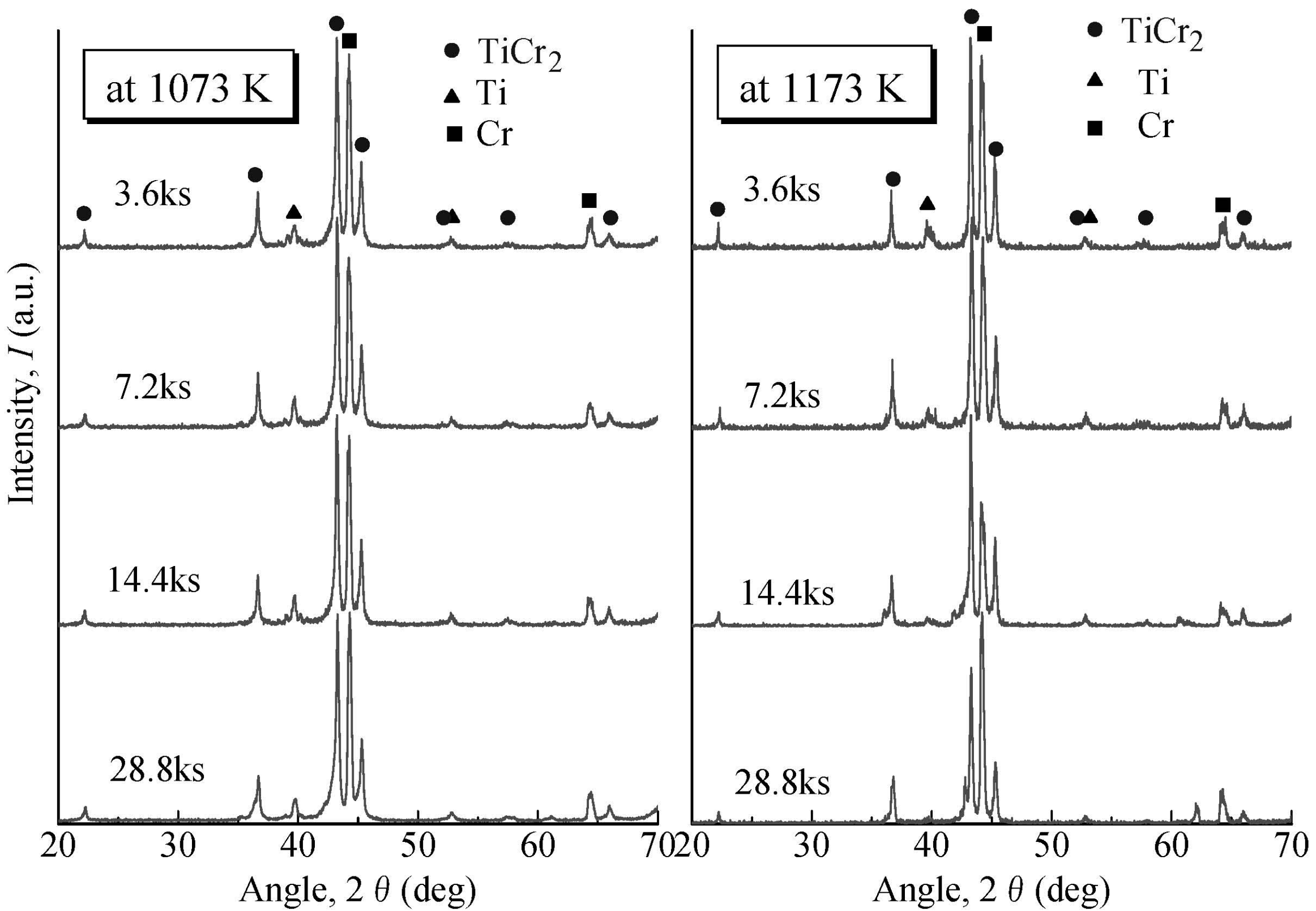


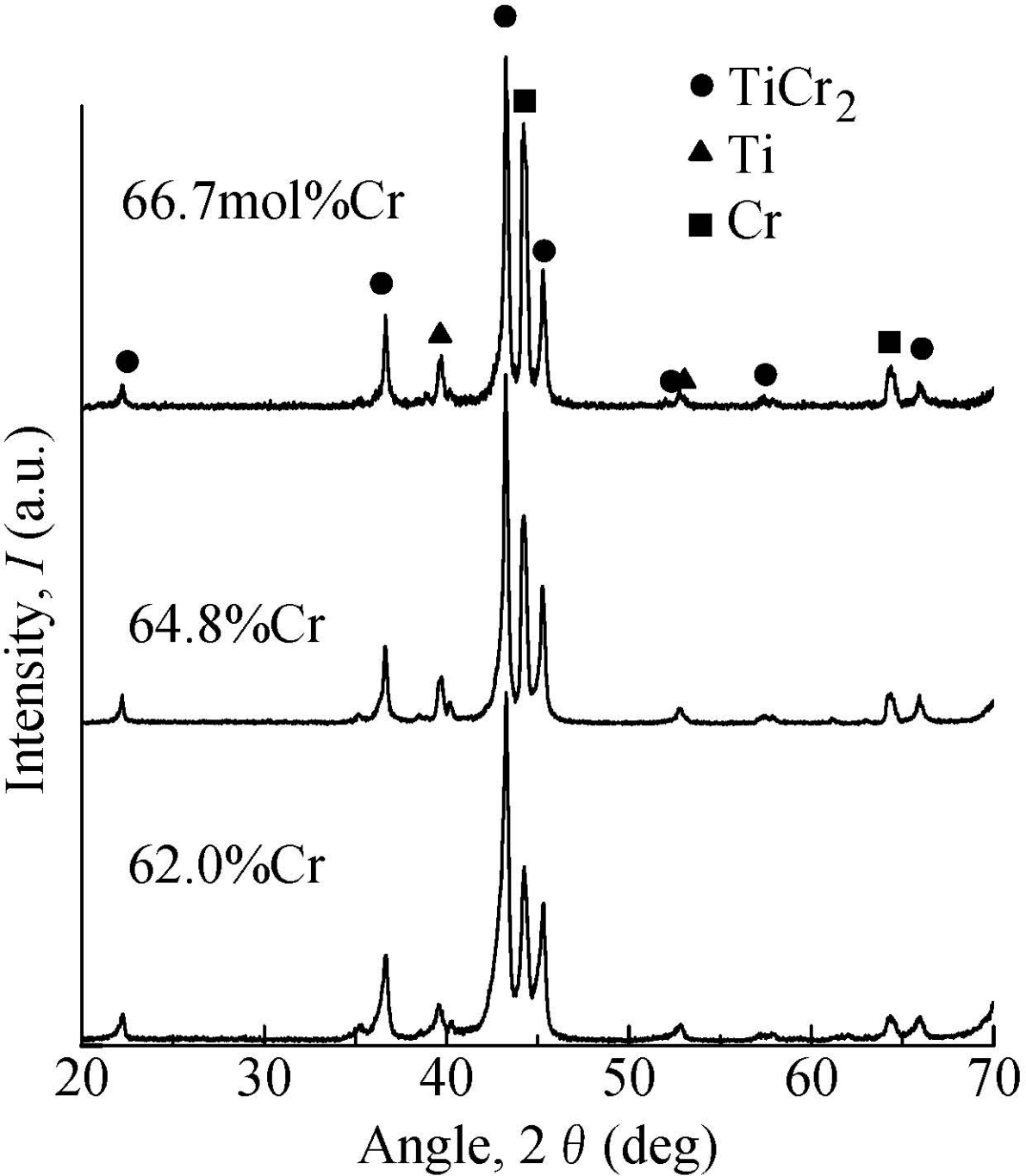
in $CaCl_2$

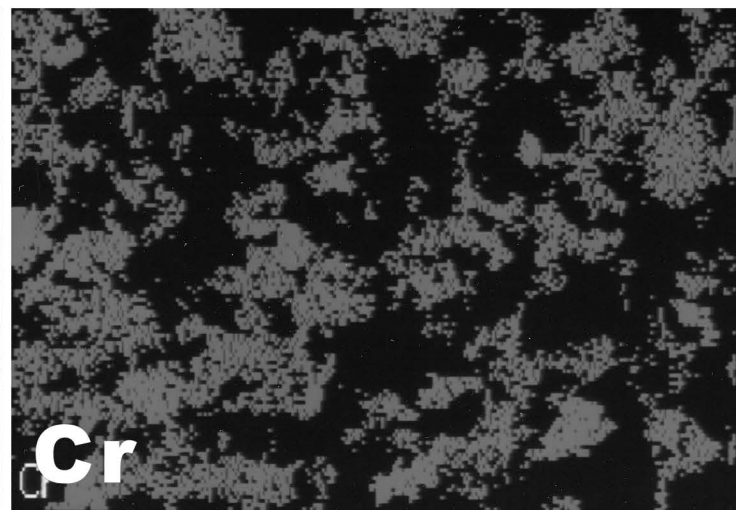
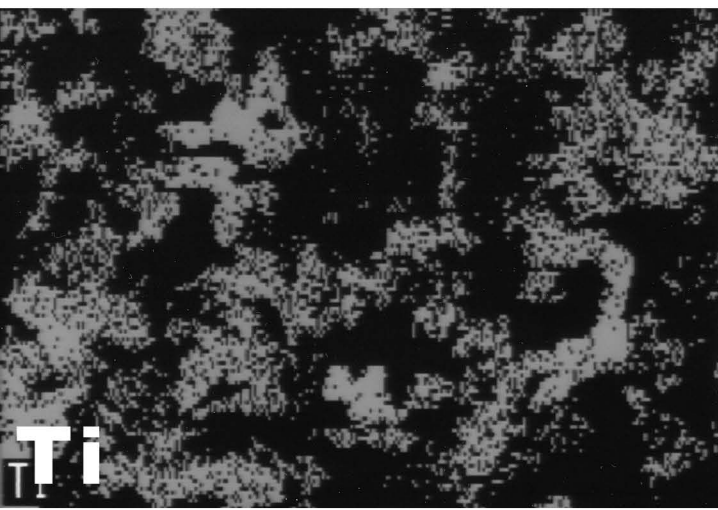
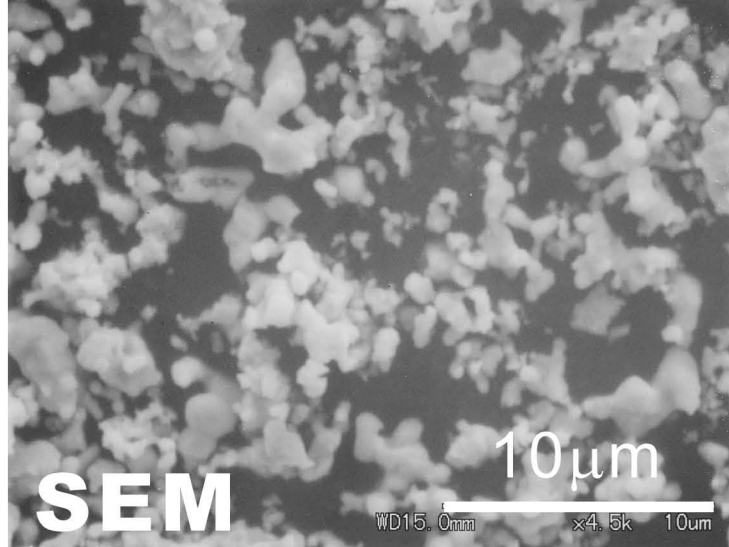


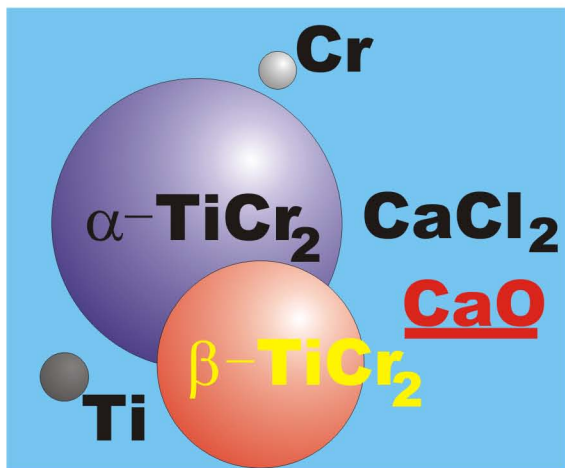
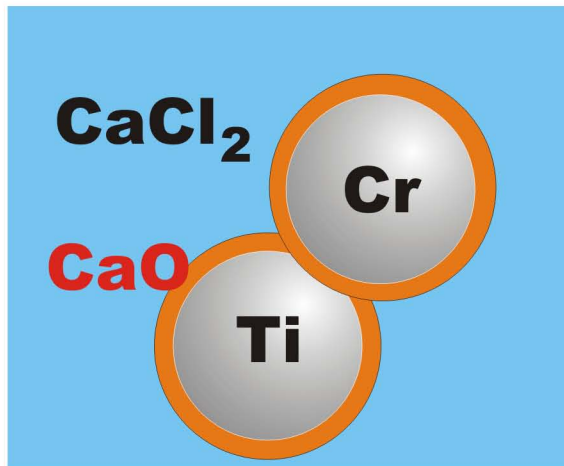
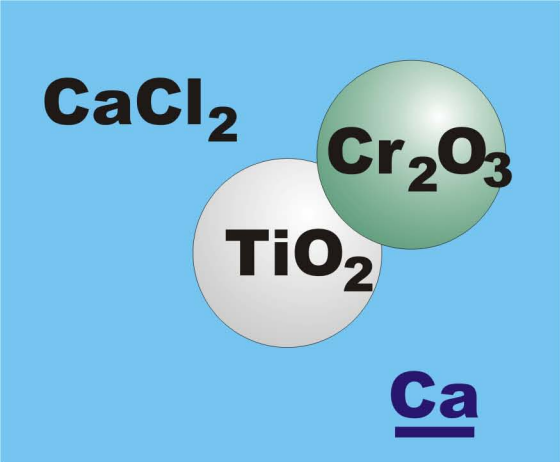




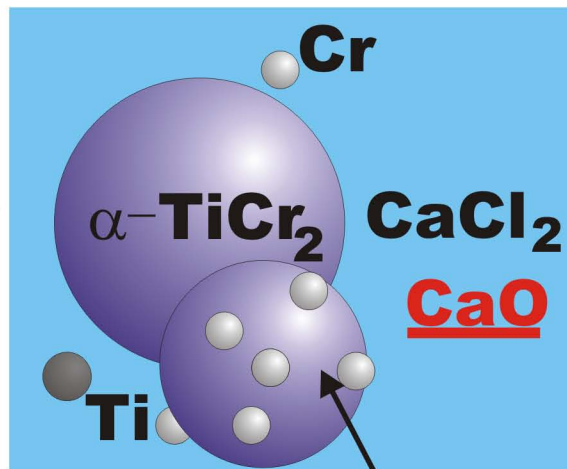








at 1173K



at RT **Cr + α-TiCr₂**

