Experimental report

28/09/2021

Proposal: 5-24-641 **Council:** 10/2019

Title: Sigma Cr-Mn phase transformation studied by in-situ temperature neutron diffraction

Research area: Materials

This proposal is a new proposal

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Samples: Cr-Mn

Instrument	Requested days	Allocated days	From	To
D1B	2	1	07/09/2020	08/09/2020

Abstract:

The phase transformation in the sigma Cr-Mn phase that has been shown only by indirect experiments in the literature will be examined in situ by high temperature neutron diffraction. The crystal structure of the new phases will be determined and refined with the Rietveld method. With the results, we plan an update of the phase diagram which is very important for steel development. Neutrons are necessary because the transition has been hypothesized as an order-disorder transition and it cannot be detected with X-ray. On the contrary, the high diffraction contrast in neutron diffraction between Cr and Mn should should allow to prove or disprove this hypothesis.

Structural transformation of the σ phase in the Cr–Mn system studied by *in situ* powder neutron diffraction

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Introduction

The thermodynamic modeling of the Cr–Mn system by the Calphad method is used for the constitution of thermodynamic databases able to predict the phase amounts and microstructures in multi-component steel systems. In this system, the σ phase deserves a special attention. It is a brittle intermetallic phase that should absolutely be avoided in commercial alloys. The structure of the σ phase is known. It is a Frank-Kasper phase containing 5 sites in the space group $P4_2/mnm$ [1]. The phase is present in many other transition metal intermetallic systems. It is characterized by a high degree of non-stoichiometry accommodated by atom mixing on the different sites of the structure. As it also exists in Cr–Fe system, its stability in Cr–Mn system and its extension into the ternary Cr–Fe–Mn system should be considered of prime interest in the frame of steel application.

However, its stability in Cr–Mn system is still matter of great uncertainty. There are reports by different experimental techniques (differential thermal analysis, magnetic susceptibility, thermal expansion) of a phase transition as a function of temperature [2]. The transition is represented in the phase diagram of Fig. 1.

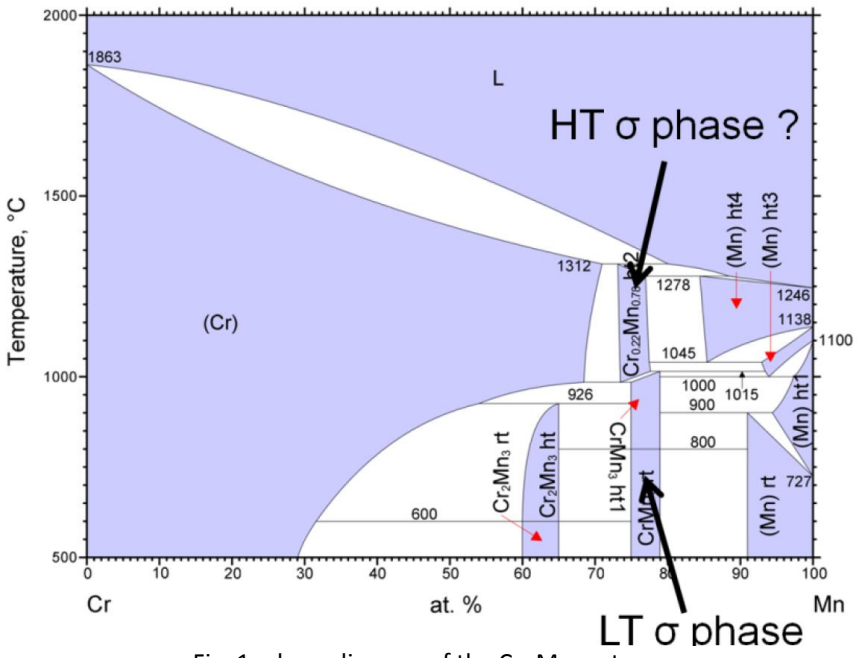

Fig. 1: phase diagram of the Cr–Mn system

The presence of a clear thermal arrest and a huge jump of the thermal expansion at ~1000°C is in favor of a first-order phase transition. As alloys quenched from the high and low temperature fields both give the same X-ray diffraction pattern of the σ phase, the transformation was thought to be an order-disorder phase transition keeping the average structure of the σ phase. From X-ray diffraction, as Cr and Mn cannot be distinguished, one can neither prove nor disprove the ordering or disordering between the two elements. On the other hand, we had carried out room temperature neutron diffraction measurements of quenched samples from the high and low temperature fields. We observed the same state of order *i.e.* no difference of site occupancies refined by the Rietveld method was detected between the samples [1] in spite of the good diffraction contrast between the two elements.

To summarize, all the techniques used up to now to study the phase transition in the σ phase are indirect techniques. They show a transition at ~1000°C but do not demonstrate the structural nature of the transition. Our structural *ex situ* neutron diffraction measurement was in contradiction with the existence of a transition. The only possibility to reconcile all the experiments was to suppose that the high temperature phase cannot be retained by quenching. It should therefore be studied by *in situ* diffraction. X-ray cannot be used due to the poor diffraction contrast between the two elements. On the contrary, neutron diffraction is perfectly adapted to the measurement of site occupancies

when Cr (*b*=3.6 fm) and Mn (*b*=-3.7 fm) are mixed. The hypothesis of a phase transition should therefore be clearly seen if it exists.

The present work is therefore reporting new *in situ* neutron diffraction experiments that have been carried out as a function of temperature for a σ phase sample.

Materials and Methods

The sample of nominal composition $Cr_{21}Mn_{79}$ has been synthesized by induction melting of the pure melting followed by two annealing treatments: one at high temperature (1100°C, one week) to homogenize the sample, one at low temperature (700°C, three weeks) to equilibrate the sample in the low temperature phase field. The sample was reduced into powder. The neutron diffraction experiment was performed at the ILL on D1B instrument remotely due to the Covid restrictions. The powder was contained in a Nb can, fitted in the high-temperature furnace. Temperature scans were programmed from room temperature up to 1200°C (heating and cooling) and the diffraction was measured as a function of temperature continuously in different temperature scans. Phases were identified and the neutron diffraction patterns were refined using the Rietveld method. This includes an accurate site occupancy refinement when the σ phase is present.

Results and Discussion

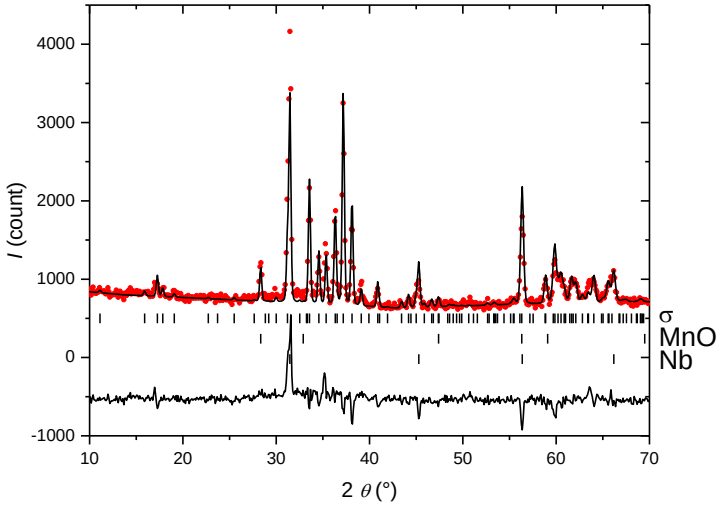

Fig. 2: Rietveld refinement of the sample at 1000°C.

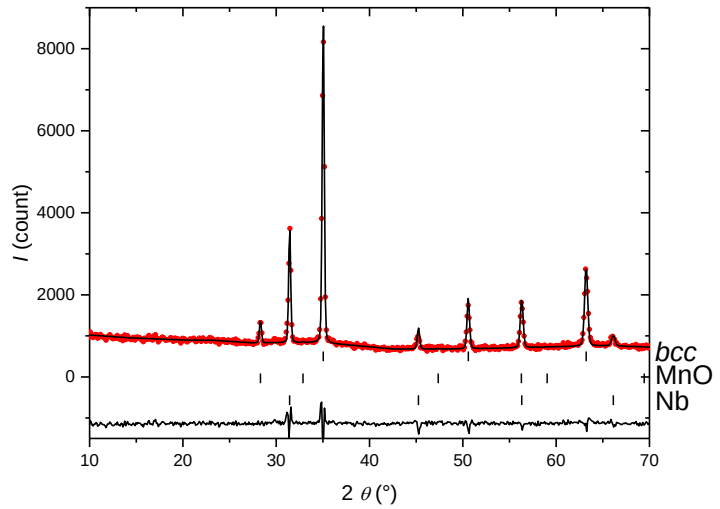

Fig. 3: Rietveld refinement of the sample at 1050°C.

The main finding of the present work was the identification of the transition occurring around 1000°C. The results show that it is not an order-disorder transition within the σ phase like previously proposed but rather a phase transition from σ to a *bcc* disordered solid solution (Figs. 2 and 3). This transformation is similar to what is present in other systems: Cr–Fe, Co–Cr, Fe–V, Mn–V…

The transformation could not be quenched *i.e.* the *bcc* phase transforms back to the σ phase at the high cooling rate of 30°C/min operated during the *in situ* experiment. This explains why this transformation could not be identified in previous work.

Site occupancies and lattice parameters were analyzed as a function of temperature (Fig. 4). The former could be compared with results from DFT calculations. This study eventually led to an update of the phase diagram.

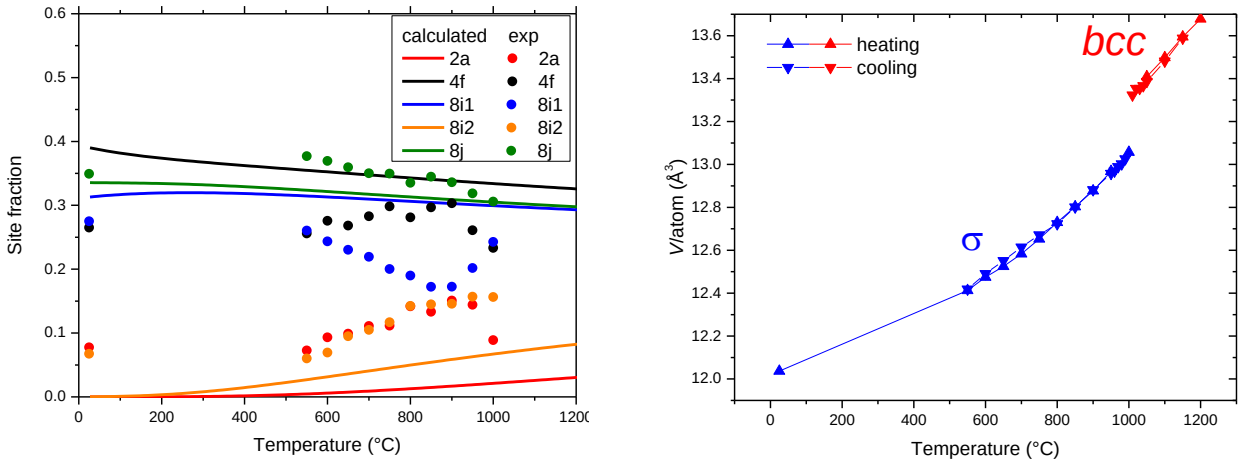

Fig. 4: Site occupancies and lattice parameters as a function of temperature. For site occupancies results from DFT calculations are also shown.

Acknowledgments
I want to thank Laetitia Laversenne local contact on D1B for her on-site help during the experiment that was done remotely.

References

[1] J.-M. Joubert, Crystal chemistry and Calphad modelling of the σ phase, Prog. Mater. Sci. **2008**, *53*, 528-583.
[2] E. Wachtel, C. Bartelt, Suszeptibilitätsmessungen im System Chrom-Mangan, Z. Met.kd. **1964**, *55 (1)*, 29-36.