Nanocrystallization of amorphous alloys using microwaves: in situ time-resolved synchrotron radiation studies

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Abstract. Important energy and time savings can be achieved with the thermal treatment of materials by replacing conventional heating methods with microwave heating. The nanocrystallization of Co-Fe-W-B amorphous alloy powders under microwave irradiation was followed for the first time by in situ time-resolved synchrotron radiation powder diffraction. It is shown that even a very short exposure to the electromagnetic field (single pulse microwave application) typically of the order of a few seconds is sufficient to obtain the bulk nanocrystalline state. A metastable high-temperature Co-W-B orthorhombic phase forms during the microwave heating, which gradually transforms to the tetragonal Co₂B stable phase.

1. Introduction
Nanocrystalline soft magnetic alloys are commonly prepared by the devitrification of amorphous alloy ribbons or powders obtained by rapid solidification or mechanical alloying, respectively. These nanomaterials are essential to a variety of modern applications, like space power generation systems, transformers, sensors, or magneto-mechanical actuators. High permeability and zero magnetostriction were among the main reasons for the extensive study of melt-spun Co-based amorphous alloys during the past [1]. Bulk Co-Fe-(Zr, Ta, Nb)-B metallic glasses were discovered by A. Inoue et al [2] which exhibit large glass-forming ability, good soft magnetic properties and ultra-high strength above 5000 MPa [3-6]. Important energy and time savings can be achieved by replacing conventional thermal treatment procedures with volumetric microwave heating [7]. The use of microwaves in the heat treatment of metal powders and alloys is relatively new and the mechanism of electromagnetic energy conversion into heat is yet unclear. It is therefore of great interest to investigate experimentally – and whenever possible in real-time - the structural and microstructural transformations induced by microwave application and their kinetics. We report on preliminary results concerning the nanocrystallization of Co-rich alloy powders as followed for the first time by in situ synchrotron radiation powder diffraction under microwave irradiation. We provide evidence for a strong enhancement of the phase transformation kinetics under microwave application and demonstrate the potential of microwave heating to modify the crystallization paths observed during conventional heating.
2. Experimental

Amorphous Co-Fe-X-B powders (X: Ta, Nb, Mo, W) were obtained by a wet-milling process, using a high-energy Retsch PM400 MA planetary ball-mill. The Co-rich alloy powders have the nominal composition Co$_{43.5}$Fe$_{20}$X$_{5.5}$B$_{31}$ and were prepared from high purity elemental powders by high-energy milling for 100 hours at 250 rotations/minute. The Co-Fe-W-B powders investigated here were loaded into sapphire capillaries and mounted in the calculated maximum E-field position of the microwave resonant cavity. The in situ microwave heating wide-angle powder diffraction experiments were performed at the MS X04SA beamline at the Swiss Light Source (SLS, Paul Scherrer Institut, Villigen, Switzerland). We have used a proprietary monomode microwave applicator operating at 2.4 GHz. More details on the experimental setup can be found in our previous papers on in situ microwave heating [8,9].

3. Results

For the acquisition of the X-ray diffraction patterns, the Mythen II detector recently developed at the SLS was used, which combines simultaneous XRD pattern acquisition within a wide angular range of up to 60°2θ with typical read-out times of 1 second. The time origin of the experiment is arbitrarily chosen. The Co-rich powders remain amorphous up to an elapsed time $t = 8$ s (figure 1). Heating is triggered by tuning the microwave cavity to the resonant position to initiate microwave absorption. No adjustments of the resonant cavity are then undertaken, the thermal evolution being further driven by the specimen alone. The pyrometer temperature first increases to 400°C (figure 2), then raises within a few seconds to 865°C. As seen in figure 2, the heating rate occasionally exceeds 110°C/second. The Co$_{53.5}$Fe$_{10}$W$_{5.5}$B$_{31}$ powders crystallize immediately upon the onset of microwave absorption (figure 1), i.e. already during the first temperature increase to 400°C ($t = 9$s). Severe overlapping of the Bragg reflections occurs, due to the large broadening of the diffraction lines of the nanocrystalline phases formed. This makes the unequivocal indexing of the diffraction patterns difficult. The following primary crystallization products were however identified (figure 1): tetragonal Co$_2$B (I4/mcm, space group SG 140, PDF 25-241), CoFe (Pm-3m, SG 221, PDF 44-1433), and the cubic Co$_{53.5}$W$_{10}$B$_{31}$ (Fm-3m, SG 225, PDF 19-372). The cooling of the specimen (figure 2) mainly occurs due to thermal dissipation processes becoming more efficient than microwave heating at high temperatures. This effect is also related to the possible thermal drift of the resonance frequency resulting in less effective or complete loss of microwave absorption.

![Figure 1](image1.png)  
Figure 1 Crystallization of amorphous CoFeWB alloy at the onset of microwave absorption.

![Figure 2](image2.png)  
Figure 2 Temperature profile recorded during the in situ microwave heating.
The high-resolution X-ray diffraction (XRD) patterns collected during ultrafast microwave heating to above 800°C are shown in figure 3. Weak traces of the residual amorphous constituent phase could be detected in the XRD patterns only up to about \( t = 12 \) s. Once the sample is fully crystallized \((t \geq 13\) s), heating becomes more efficient and the sample rapidly reaches 865°C (within 5 s). This sudden increase of the heating rate also indicates a better microwave absorption upon complete crystallization.

The amorphous \( \text{Co}_{53.5}\text{Fe}_{10}\text{W}_{5.5}\text{B}_{31} \) powders crystallize into a complex mixture of tetragonal \( \text{Co}_2\text{B} \) (lattice parameters \( a = 0.50522 \pm 0.00007 \) nm, \( c = 0.42281 \pm 0.00008 \) nm), cubic \( \text{CoFe} \) \( (a = 0.28549 \pm 0.00026 \) nm), cubic \( \text{Co}_2\text{W}_2\text{B}_6 \) \( (a = 1.05255 \pm 0.00023 \) nm) and orthorhombic \( \text{CoWB} \) (Pnma, SG 62, PDF 23-124, lattice parameters \( a = 0.57339 \pm 0.00069 \) nm, \( b = 0.32463 \pm 0.00046 \) nm, \( c = 0.66299 \pm 0.00055 \) nm), as shown in figure 4 (corresponds to an elapsed time \( t = 23 \) s).

The evolution of the volume fractions of \( \text{Co}_2\text{B} \) (triangles) and \( \text{CoWB} \) (squares) phases during microwave exposure. The \( \text{CoWB} \) phase is metastable, and transforms to tetragonal \( \text{Co}_2\text{B} \).
Upon conventional heating, the main primary crystallization product is the metastable Co$_{21}$W$_2$B$_6$ phase [3,10], which tends to decompose into stable CoB and Co$_3$B$_2$ phases upon high-temperature annealing. The cubic CoFe phase is often also present as additional primary crystallization product. At difference to this result, in microwave heating we could evidence the additional formation of the tetragonal Co$_2$B phase already during the initial stage of nanocrystallization. Moreover, in the present microwave experiments the orthorhombic CoWB ternary phase forms at a much lower temperature than observed in conventional heating (about 725°C, [11]). We may consequently conclude that in microwave heating the crystallization path is modified compared to the case of conventional heat treatment. A preliminary evaluation of the relative fractions of these two constituent phases is shown in figure 5. This first evaluation of the crystalline fractions of the Co$_2$B and CoWB phases clearly shows that the orthorhombic CoWB phase is metastable, and that it gradually transforms into the tetragonal Co$_2$B phase. A more detailed analysis of the experimental data, including the microwave crystallization of CoFeTaB and CoFeNbB amorphous powders, is in progress.

4. Conclusions

The increasing availability of synchrotron radiation sources and the tremendous progress registered with the development of ultrafast detectors but also with monitoring of microwave heating processes in general [12], enabled experiments in which the structural and microstructural evolution of solids under microwave application can be accurately followed in near to real-time conditions. Information yielded by *in situ* time-resolved experiments is awaited to improve our knowledge on the mechanisms of mass transport and structural phase transitions in the presence of electromagnetic fields.

The microwave-induced crystallization of amorphous Co$_{53.5}$Fe$_{10}$W$_{5.5}$B$_{31}$ alloy powders obtained by high-energy ball milling was followed for the first time by *in situ* time-resolved synchrotron radiation powder diffraction. Following the onset of microwave absorption, the amorphous Co-rich powders instantly crystallize into a complex mixture of cubic CoFe, tetragonal Co$_2$B, face-centered-cubic Co$_{21}$W$_2$B$_6$ and orthorhombic CoWB phases. The Co$_2$B is not a primary crystallization product in the conventional heat treatment of this alloy. Also, the formation of orthorhombic CoWB phase is observed at much lower temperatures than in conventional heating. The CoWB phase is metastable and gradually assumes the tetragonal Co$_2$B structure. This clearly indicates the potential of microwave heating in modifying conventional crystallization paths, in offering access to metastable phases and thus to new properties. In agreement with the results of similar *in situ* experiments recently performed on amorphous Finemet-type alloys [9], the transformation kinetics is orders of magnitude higher than in conventional heating. This enhancement can be understood by taking into account Joule heating effects but also the rapid conversion of electromagnetic energy into heat via local spin reorientation and domain wall propagation processes.

References

[1] McHenry M E, Willard M A and Laughlin D E 1999 *Progress in Materials Science* 44 291
[2] Inoue A 2000 *Acta Materialia* 48 279
[3] Inoue A, Shen B L, Koshiba H, Kato H and Yavari A R 2003 *Nature Materials* 2 661
[4] Inoue A, Shen B L, Koshiba H, Kato H and Yavari A R 2004 *Acta Materialia* 52 1631
[5] Shen B L and Inoue A 2005 *J. Phys: Cond Matter* 17 5647
[6] Inoue A, Shen B L and Chang C T 2006 *Intermetallics* 14 936
[7] Sanchez-Hernandez D and J.M. Catalá-Civera 2006 *Advances in Microwave and Radio Frequency Processing* ed M. Willert-Porada (Springer Verlag, Berlin) pp. 92-102
[8] Vaucher S, Nicula R, Català-Civera J M, Schmitt B, Patterson B 2008 *J. Mater. Res.* 23 171
[9] Nicula R, Stir M, Ishizaki K, Català-Civera J M and Vaucher S 2009 *Scripta Mater.* 60 120
[10] Kanasz R, Bednarcik J, Saksl K, Nicula R, Stir M, Lathe C 2008 *Acta Phys. Pol. A* 113 79
[11] Bednarcik J 2008 private communication.
[12] Vaucher S and Nicula R 2008 *Chemistry Today* 26 38