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14. ABSTRACT

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RPPR Final Report

as of 21-Mar-2022

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INVESTIGATOR(S):

Name: Bryan Webler
Email: Webler@cmu.edu
Phone Number: 4122682675
Principal: Y

Organization: **Carnegie Mellon University**

Address: Associate Director, Sponsored Programs, Pittsburgh, PA 152133890

Country: USA

DUNS Number: 052184116

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Final Report for Period Beginning 15-Dec-2017 and Ending 14-Jan-2022

Title: Fabrication of Metal/Oxide Composites via Internal Oxidation & Severe Plastic Deformation

Begin Performance Period: 15-Dec-2017

End Performance Period: 14-Jan-2022

Report Term: 0-Other

Submitted By: Bryan Webler

Email: Webler@cmu.edu

Phone: (412) 268-2675

Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1

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Major Goals: The major goal of this project has been to investigate a bulk processing route for producing metal/oxide composite materials via a combination of internal oxidation and equal channel angular pressing (ECAP) of bulk Fe-based alloys. Some important factors that we have identified in creating a material that is a viable candidate for real-world applications are the internal oxidation depth and the post-ECAP microstructure. We have concentrated our efforts on optimizing the alloy compositions, oxidation conditions, and ECAP process variables in order to produce an alloy with maximized internal oxidation depth and a post-ECAP microstructure with ultrafine grains and dispersed oxides. There were two tasks:

(1) Obtain the deepest possible internal oxidation - Vary alloy composition, temperature, and oxidizing atmosphere to internally oxidize Fe-Y alloys. These alloys exhibit in-situ internal oxidation. Examine oxidized microstructure and characterize initial oxide size and morphology.

(1) Examine microstructure evolution after ECAP - Perform ECAP and study the change in alloy microstructure and distribution of oxides. Measure changes to mechanical behavior after ECAP and after annealing (to assess thermal stability). Assess if ECAP can be used to distribute the oxides through the microstructure.

Accomplishments: This work investigated the processing of metal/oxide composites by internal oxidation of a bulk alloy, followed by severe plastic deformation for grain size refinement and oxide dispersion. Internal oxidation rates have been shown to be exceptionally high in alloys exhibiting in situ oxidation. Referred to as a "diffusionless" or "in-situ" internal oxidation, this accelerated oxidation process occurs in materials where the reactive solute phase has negligible solubility and diffusivity in the matrix. The Fe-Y binary system was initially chosen for this study for its in situ internal oxidation characteristics and similarity in composition to metal/oxide composites that are traditionally processed with Fe-based alloys and Y-rich oxides. As a complement to the Fe-Y system, Fe-Zr-Y alloys were also investigated as a candidate for internally oxidized metal/oxide composites. The oxidation behavior of Fe-Zr-Y alloys has not yet been reported in the literature, but ternary Ni-Zr-Y alloys have been known to undergo rapid in situ internal oxidation.

The first stage of this study was the characterization of Fe-Y alloys containing 1.5 wt.% yttrium that were internally oxidized at 800C and deformed using ECAP route BC (alloy samples were inserted into pure Fe billets for ECAP at 25°C and 350°C). The post-ECAP microstructure was examined, and an automated technique was developed to analyze particle dispersion in these deformed alloys. Based on the characterization of these previously made alloys, a new experimental procedure was designed for the internal oxidation and ECAP deformation of Fe-Y and Fe-Zr-Y alloys to form metal/oxide composites. The as-cast microstructure of the Fe-Y alloy is shown in Figure 1 (a). The dark gray matrix is pure iron and there is Fe₁₇Y₂ phase in the interdendritic regions. Both oxidized and unoxidized regions were broken up after ECAP, Figure 1(b), but there was no bulk redistribution of the intermetallic

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or oxide phase. A high-throughput automated image analysis program was developed to quantify particle dispersion. No significant change in dispersion with processing conditions was found in the unoxidized region. In the oxidized region, there was no change in dispersion with number of passes, but the room temperature samples had lower skewness values (i.e., more dispersed) than their respective high temperature samples. However, the extent of the difference was not very high. For future experiments it was recommended to try a different ECAP route to better disperse the oxides and to obtain a deeper internally oxidized layer. There were also no differences in grain size (Figure 1(c)) or nanohardness (including after high temperature holds) (Figure 1(d)).

To address internal oxidation depth, the effect of Zr additions was investigated (Zr led to very rapid oxidation in the Ni-Y-Zr system). A new set of alloys was created using a laboratory scale arc-melting furnace, Fe – 3wt% Y and Fe – 2.68 wt% Zr – 0.38 wt% Y. The as-cast Fe-Y microstructure consisted of a pure Fe matrix with Fe₁₇Y₂ intermetallic structure, while the Fe-Zr-Y alloys were found to have an Fe matrix with a multiphase secondary structure including Fe₂Zr and Y-stabilized Fe₂₃Zr₆ (see Figure 2(a)). Alloys were oxidized in air using a thermogravimetric analysis (TGA) furnace at 800C, 1000C and 1200 C for 1.5 to 12 hours. The new set of Fe-Y alloys experienced internal oxidation up to twice as deep as the previously studied Fe-1.5 wt.% Y alloys, forming bundles of rodlike oxides at the oxidation front which coarsened into bands of discrete globular particles over time (Figure 2(b) and (c)). The oxide structure of the Fe-Zr-Y was very different from the Fe-Y alloys, forming an interconnected oxide network (Figure 2(c)). The depth of internal oxidation in Fe-Zr-Y was always greater than Fe-Y and was through-thickness at 1000C and 1200C.

To better understand the microstructure and oxidation behavior of Fe-Zr-Y materials, a new set of ternary alloys was produced with varied Zr/Y ratios (compositions listed in Table 1). The as-cast alloys were found to have a multiphase secondary structure featuring FeZr₂ and Fe₂₃Zr₆, the latter with some dissolved Y. As-cast microstructures are shown in Figure 3(a). The amounts of each phase present depended on alloy composition. These alloys were oxidized at 800C, 1000C and 1200C for three hours under N₂ - 5%H₂ gas with a controlled dew point of 0C. The internally oxidized microstructures also exhibited both Zr-rich and Y-rich phases in similar distributions to the as-cast alloys, indicating that internal oxidation occurred by an in-situ process, Figure 3(b). As shown in Figure 3(c), all ternary Fe-Zr-Y alloys exhibited significantly higher oxidation rates and internal penetration depths greater than twice the values of the binary Fe-Zr or Fe-Y alloys. Peak internal oxidation rates were observed in the 2ZY4 alloy, which had the lowest Y content of the Fe-Zr-Y alloys studied. Slower oxidation of the Y-rich phase likely caused decreased oxidation rates in the higher-Y alloys. The variation of internal oxidation rate with composition correlated with the variation of oxygen diffusivity with composition in yttria-stabilized zirconia (YSZ). In these ternary alloy systems, the oxidation mechanism is oxygen diffusion through the YSZ oxide phase.

A new ECAP procedure was developed for the oxidized Fe-Y and Fe-Zr-Y alloys. The use of back pressure (applied load on the head end of the specimen as it is passed through the ECAP die) was found to successfully mitigate surface cracking, see Figure 4(a). Internally oxidized Fe-Y and Fe-Zr-Y alloys were encased in pure Fe billets and deformed via ECAP Route A for four passes. The post-ECAP microstructure shown in Figure 4(b) and (c) revealed that there was no redistribution of oxide particles into the matrix. Rather, oxides remained clustered together in bands, and the oxide bands underwent stretching and reshaping within the deformed alloy microstructure, indicating that the effect of ECAP on particle dispersion is highly dependent on original microstructure length scale. Further progress on manipulating original microstructure length scale and more detailed investigation of ECAP was limited by COVID-19 pandemic restrictions.

Training Opportunities: There was one PhD student who was responsible for the day-to-day activities of this project. During the project, the student had numerous training opportunities, particularly in electron microscopy. The student also attended and presented at three conferences: Materials Science & Technology (MS&T) 2017, The TMS Annual Meeting 2018, the Microscopy & Microanalysis Society Annual Meeting in 2018, and MS&T 2019.

The student also attended several professional development seminars:
10/08/2018 - "PhD Career Pathways", Microscopy Society of America
02/12/2019 - "Time Management, Productivity and Motivation", CMU Academic development
05/28/2019 - "Communicating Science Professionally", Microscopy Society of America

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Results Dissemination: The results were disseminated at conferences and in the student's (Anna Mian) published PhD thesis:

MS&T 2017 - "Severe plastic deformation effects on nanoscale oxide dispersion of internally oxidized Fe-Y alloys"

TMS 2018 - "Effect of nanoscale oxide dispersion on thermal stability of severely deformed Fe-Y alloy"

Microscopy & Microanalysis 2018 - "Characterizing the effect of ECAP on particle dispersion and thermal stability of internally oxidized Fe-Y alloys"

MS&T 2019 "Characterizing Metal Oxide Composites Processed by Internal Oxidation and Severe Plastic Deformation"

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI

Participant: Bryan Arthur Webler

Person Months Worked: 1.00

Project Contribution:

National Academy Member: N

Funding Support:

Participant Type: Co PD/PI

Participant: Yoosuf Neelam Picard

Person Months Worked: 1.00

Project Contribution:

National Academy Member: N

Funding Support:

Participant Type: Co-Investigator

Participant: Jorg Michael Wiezorek

Person Months Worked: 1.00

Project Contribution:

National Academy Member: N

Funding Support:

Participant Type: Graduate Student (research assistant)

Participant: Anna Christine Mian

Person Months Worked: 12.00

Project Contribution:

National Academy Member: N

Funding Support:

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CONFERENCE PAPERS:

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: TMS Annual Meeting
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Conference Location: Phoenix, Arizona
Paper Title: Effect of nanoscale oxide dispersion on thermal stability of severely deformed Fe-Y alloy
Authors: Anna Weiss, Yoosuf Picard, Bryan Webler
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: Microscopy and Microanalysis 2018 Meeting
Date Received: 30-Aug-2019 Conference Date: 05-Aug-2018 Date Published:
Conference Location: Baltimore, MD
Paper Title: Characterizing the Effect of ECAP on Particle Dispersion and Thermal Stability of Internally Oxidized Fe-Y Alloys
Authors: Anna Weiss, Yoosuf Picard, Bryan Webler
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: Materials Science and Technology 2019
Date Received: 18-Mar-2022 Conference Date: 30-Sep-2019 Date Published:
Conference Location: Portland, Oregon, USA
Paper Title: Characterizing metal oxide composites processed by internal oxidation and severe plastic deformation
Authors: Anna Weiss, Jorg Wieszorek, Yoosuf Picard, Bryan Webler
Acknowledged Federal Support: **Y**

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Title: Internal Oxidation and Equal Channel Angular Pressing of Fe-Y and Fe-Zr-Y Alloys
Authors: Anna Mian
Acknowledged Federal Support: **Y**

Partners

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as of 21-Mar-2022

I certify that the information in the report is complete and accurate:

Signature: Bryan A Webler

Signature Date: 3/18/22 1:51PM

Figure 1 – Results from characterization of Fe 1.5 wt% Y samples after ECAP.

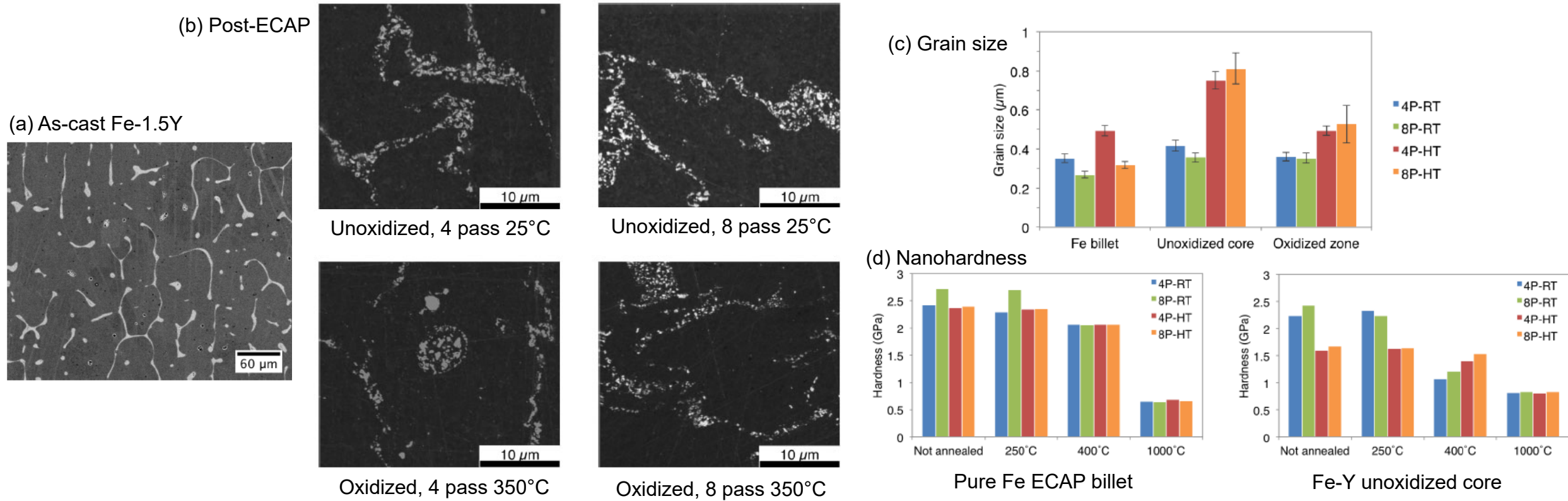
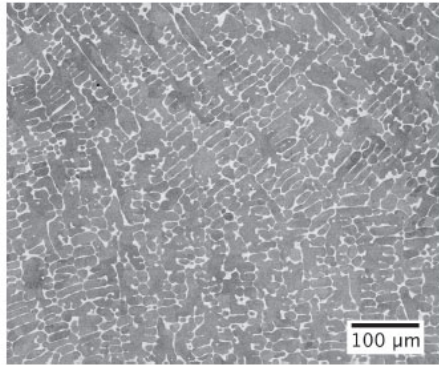
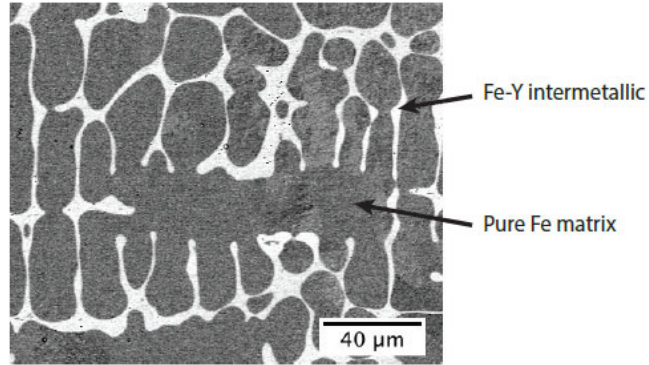


Figure 2 – Results of internal oxidation experiments in air on Fe-Y and Fe-Zr-Y alloys

(a) As-cast Fe-Y and Fe-Zr-Y alloys

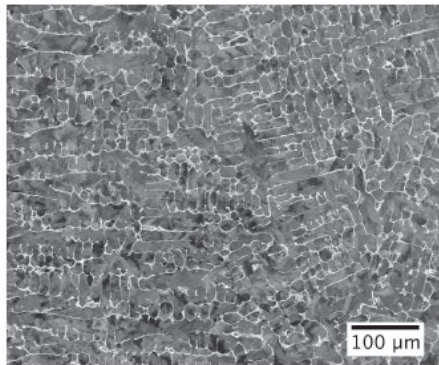
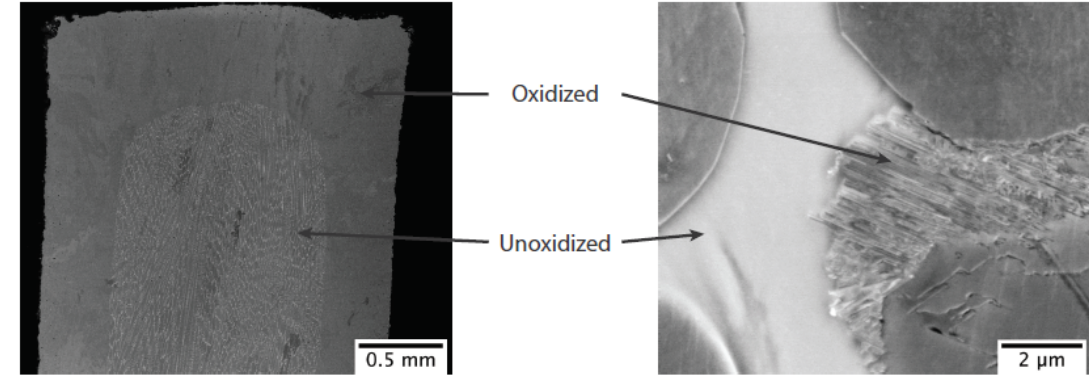


(a) Fe-Y, low magnification

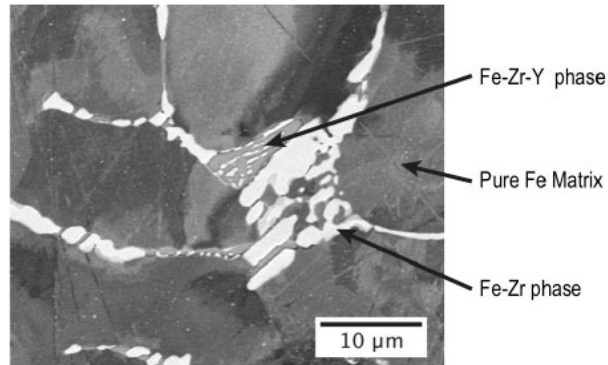


(b) Fe-Y, high magnification

(b) Low and high magnification images of internally oxidized Fe-Y

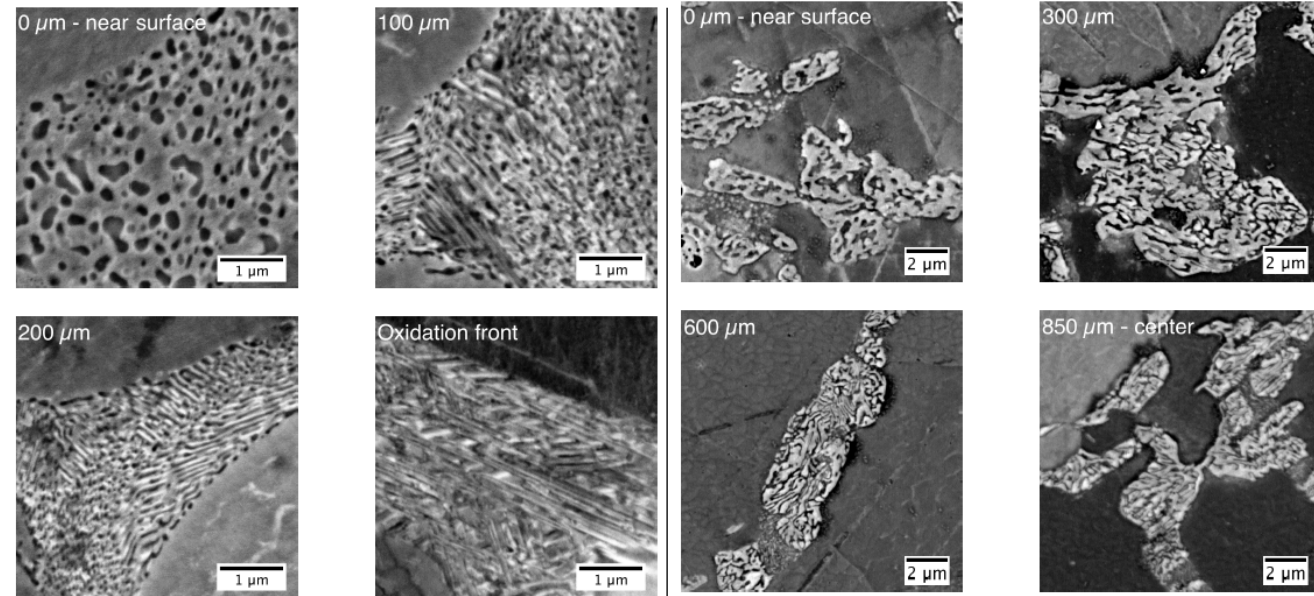


(c) Fe-Zr-Y low magnification



(d) Fe-Zr-Y high magnification

(c) Oxidized microstructures at different distances from the surface



Fe - Y

Fe - Zr - Y

Table 1 – Chemical composition of Fe – Zr, Fe – Zr – Y, and Fe – Y alloys fabricated for internal oxidation with controlled dewpoint experiments.

Y_2O_3	2Z 0 %	2ZY4 4 %	2ZY8 8 %	2ZY12 12 %	2ZY16 16 %	2ZY30 30 %	2Y 100 %
at.% Fe	98	98	98	98	98	98	98
at.% Zr	2	1.85	1.70	1.57	1.46	1.08	0
at.% Y	0	0.15	0.30	0.43	0.55	0.92	2
wt.% Fe	96.77	96.78	96.79	96.79	96.80	96.81	96.9
wt.% Zr	3.23	2.98	2.75	2.54	2.34	1.74	0
wt.% Y	0	0.24	0.47	0.67	0.87	1.45	3.15

Figure 4 – Results of Fe – Zr, Fe – Zr – Y, and Fe – Y internal oxidation with controlled dewpoint experiments.

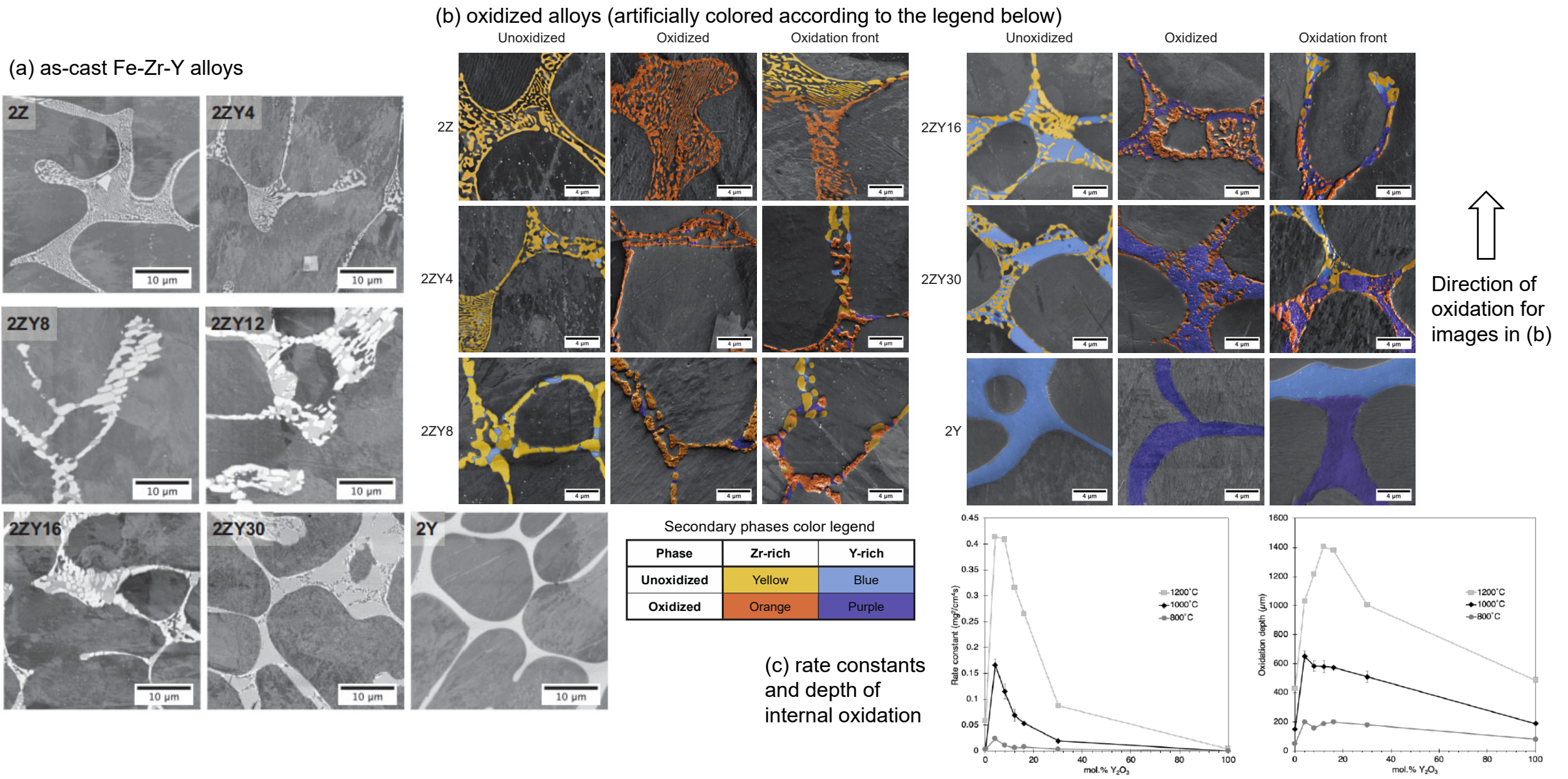


Figure 5 – Results of ECAP tests on Fe – Y and Fe – Zr – Y

(a) Mitigation of cracking with backpressure

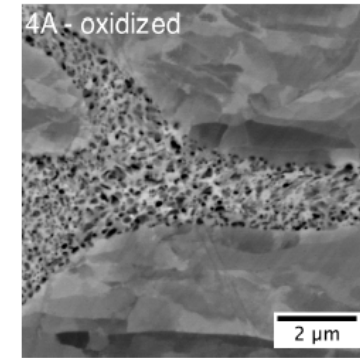
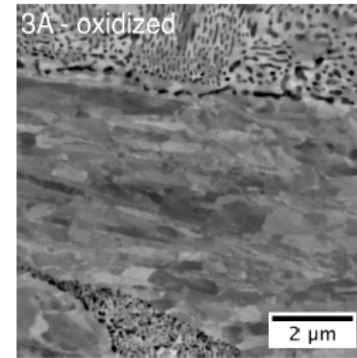
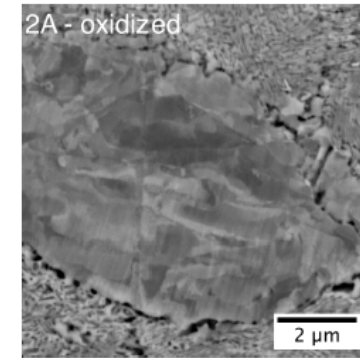
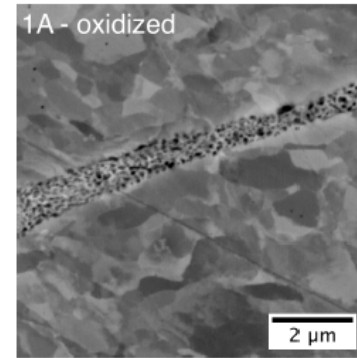


(a) Before ECAP

(b) 1P: no back pressure

(c) 1P: with back pressure

(b) Fe-Y



(# on these figures is # passes using ECAP route A)

(c) Fe-Zr-Y

