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Microstructure and phase investigation of FeCrAl- Y_2O_3 ODS steels with different Ti and V contents

Jaroslaw J. Jasinski ^{a,b}, Tomasz Stasiak ^{a,*}, Wojciech Chmurzynski ^a, Lukasz Kurpaska ^{a,b}, Marcin Chmielewski ^{a,c}, Malgorzata Frelek-Kozak ^{a,b}, Magdalena Wilczopolska ^b, Katarzyna Mulewska ^{a,b}, Maciej Zielinski ^b, Marcin Kowal ^a, Ryszard Diduszko ^{b,c}, Witold Chrominski ^{b,d}, Jacek Jagielski ^{a,b}

^a National Centre for Nuclear Research, Materials Research Laboratory, A. Soltana 7 St., 05-400 Otwock-Swierk, Poland

^b National Centre for Nuclear Research, Centre of Excellence NOMATEN, A. Soltana 7 St., 05-400 Otwock-Swierk, Poland

^c Lukasiewicz Research Network, Institute of Microelectronics and Photonics, Wolczynska 133St., Warsaw 01-919, Poland

^d Faculty of Materials Science and Engineering, Warsaw University of Technology, Woloska 141 St., Warsaw 02-507, Poland

HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- FeCrAl-Y₂O₃ ODS alloys were fabricated for applications in GenIV nuclear reactors.
- The mechanically alloyed powders show good chemical homogeneity.
- The spark plasma sintered samples reveal good densification and bcc phase matrix.
- Nanometric reinforcing particles (15–50 nm) are homogeneously distributed.
- The alloy with the addition of vanadium shows improved mechanical properties.

ARTICLE INFO

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ABSTRACT

FeCrAl-based steels are considered promising materials for high-temperature nuclear applications. Over the past years, various compositions have been studied to assess their mechanical properties, structural integrity, and radiation damage resistance. However, the microstructure and phase composition of FeCrAl-ODS steels with the addition of different alloying elements are less commonly studied than pure FeCrAl alloys. The paper presents a novel research path for developing FeCrAl matrix ODS steels with Y_2O_3 , Ti, and V additions. The materials synthesis consisted of mechanical alloying of pure metallic components with yttrium oxide in a planetary ball mill under an argon atmosphere. Titanium was added in the amount of 1.0 wt.% to both samples, while 0.5 wt.% of vanadium was added to one sample to verify its impact on the structural stability and hardness. The spark plasma sintering (SPS) technique was used to consolidate the powders. Afterward, the microstructure, chemical composition, phase composition, and hardness were assessed using SEM-EDS, EBSD, TEM-EDS, XRP, Nanoindentation, and Vickers microhardness. The experimental data reveal rather homogeneous powders after mechanical alloying and dense bulk samples after SPS. The microstructure observations show oxide particles and carbides on the grain boundaries and inside grains of the bcc matrix, which suggests elevated radiation damage resistance. The presence of nanoscale oxide particles (15–50 nm) in the matrix could significantly reduce the

* Corresponding author.

E-mail address: tomasz.stasiak@ncbj.gov.pl (T. Stasiak).

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impact of aging embrittlement at high temperatures by affecting the chromium diffusion pathways in the ODS steel matrix. The addition of vanadium leads to an improvement of hardness to 4.83 ± 0.43 GPa compared to 3.78 ± 0.34 GPa for the sample without vanadium. Presented experimental results are promising in terms of research and development of FeCr and Al-based ODS materials tailored to operate under harsh conditions in generation IV fission reactors and fusion reactors.

1. Introduction

Nuclear power plants and renewable energy sources could significantly lower the carbon footprint of electricity production and satisfy the continuous increase in energy demand worldwide. Therefore, there is a constant need to develop novel advanced materials for the nuclear power industry. Among many other promising materials, FeCrAl ferritic alloys with different content of Cr and Al are studied extensively for industrial and nuclear component applications [1-5]. They present better oxidation and corrosion resistance than Fe-Cr alloys due to the growth of the surface's passive alumina (α -Al₂O₃) layer [2]. However, the limitation of these alloys is a relatively low operating temperature, which is insufficient for designing new nuclear reactor elements. Another disadvantage of these alloys could be embrittlement at 475 °C, which is a common effect in Fe-based alloys containing a high amount of Cr, usually above 12 wt.%, due to α (Fe-enriched) and α ' (Cr-enriched) phase separation. Nevertheless, it seems that alloys with a lower content of Cr are less susceptible to thermal aging embrittlement [6]. Moreover, the Al addition's role is also often discussed, but firm conclusions have not been made yet. A higher amount of Al could prevent α - α ' phase separation, while a low Al amount could enhance the phase separation [7,8]. In addition, Al also stabilizes ferrite in Fe-based alloys with Cr content lower than 12 wt.% [6]. Moreover, the Al addition could improve corrosion resistance in lead-bismuth eutectics and supercritical water, which is essential in the design of Generation IV reactors [9–12]. However, the Al addition could decrease high-temperature strength [9, 13].

To improve mechanical properties, mainly creep resistance, and yield strength, while improving high temperature corrosion resistance, a good solution could be strengthening the FeCrAl alloy matrix with oxide particles and carbides [14,15]. For this reason, in this study, we propose enriching developed FeCrAl-based steels with Ti and V (maximum 1 and 0.5 wt.%) and Y₂O₃. These metallic elements are also well known as responsible for steels microstructure strengthening (Vanadium [16,17]) and improving their corrosion resistance (Titanium [18]). The development of oxide dispersion-strengthened (ODS) alloys has been studied for many years so far with excellent results [19,20]. The mechanical alloying route is relatively well-known and considered the next method to produce materials combining unique properties [21,22]. ODS alloys often consist of ferritic or ferritic/martensitic matrix and oxides dispersed in the matrix [23]. They contain Fe as a base element and usually have a high content of Cr to improve corrosion resistance [24]. ODS alloys present many exceptional properties, such as high radiation resistance, good mechanical properties, including creep resistance, high yield strength at high temperatures, and low activation [25-27]. These properties positively affect the microstructure of most produced ODS alloys (fine grains and high dislocation density) and the dispersed oxide particles, which hinder grain boundary migration and dislocation glide [28]. In addition, complex oxide nanoparticles act as trapping sites for point defects produced during neutron irradiation [29]. Moreover, oxide precipitates in the FeCrAl matrix could significantly delay α - α ' phase separation and prevent thermal aging embrittlement, as mentioned [30, 31]. Therefore, ODS alloys, especially with FeCrAl matrix, are promising candidates for operation in harsh environments, including nuclear reactors, where materials are expected to withstand high temperature (even up to 700 °C), intensive radiation (severe neutron displacement damage up to 200 dpa), complex force field or corrosive coolants without the possibility of frequent replacement. The most promising application of FeCrAl alloys is for fuel cladding applications in the next-generation super-critical water-cooled reactor (SCWR) [32,33] and boiling water reactors (BWR) [34]. For this reason, water-cooled small module reactors (SMRs), such as BWRX-300 and NuScale, are potential reactors for the FeCrAl-ODS fuel cladding to enhance safety margins, fuel efficiency, and economics [35]. However, ODS FeCrAl alloys are studied less extensively than pure FeCrAl alloys [9,11,14,36–39]. So, very limited publication record encourages the investigation of these alloys and their manufacturing.

The most common fabrication technique for ODS alloys is powder metallurgy [19,37,40,41]. It consists of mechanical alloying (MA), which was invented initially to produce ODS superalloys [42]. The raw elemental metallic powders and oxide powder (i.e., Y2O3) are milled in a high-energy ball mill device to obtain a rather homogeneous powder mixture [42]. As a solid-state technique, mechanical alloying presents many advantages over liquid methods, such as extended solubility of elements, no casting segregation, or no problem with significantly different melting temperatures with the preparation of alloys consisting of many elements [42,43]. However, the most important advantage is the fabrication of powder with a fine grain structure, which positively affects the mechanical properties of bulk material [42-44]. The most common powder consolidation methods of ODS alloys are hot isostatic pressing (HIP) [28,40,45] and hot extrusion (HE) [36,40,45,46]. In addition, during sintering, the complex oxides are precipitated from oxide particles (e.g., Y2O3) decomposed during mechanical alloying and from matrix elements with high affinity to oxygen, such as Al, Ti, etc. [29,47]. Although less frequently used to produce bulk ODS alloys than HIP and HE, also an up-and-coming technique is spark plasma sintering (SPS) [37,48,49]. The microstructure produced by SPS usually consists of equiaxed grains without any texture [37,40]. Short-time heating in the SPS method enables almost full densification and obtaining complex nano-sized oxides (which favors high mechanical properties). This method prevents nanoparticle coarsening and excessive grain growth, enabling the preparation of bulk samples with matrix grain size usually below 1 µm [40]. However, short-time sintering does not allow much diffusion to homogenize materials; therefore, the chemical homogeneity after mechanical alloying seems more critical [40].

In conclusion, the paper aims to investigate the possibility of preparing ODS FeCrAl alloys with the addition of Y_2O_3 , Ti, and V by powder metallurgy techniques, i.e., mechanical alloying followed by SPS consolidation. Moreover, the role of alloying elements Ti and V content and Y_2O_3 oxide particles on microstructure homogeneity and hardness was studied. The presented study is at its preliminary stage of research. However, promising results convinced us to present the first outcomes from the initial characterization campaign.

2. Materials and methods

2.1. Mechanical alloying and consolidation process

The FeCrAl-ODS steels samples of two different compositions shown in Table 1 were prepared using powder metallurgy techniques involving MA followed by SPS.

The high-purity powders for mechanical alloying were commercially purchased from Alfa Aesar: Fe (purity 99.9% metal basis, $C \le 0.2\%$, $O \le 0.4\%$), Cr (purity 99.99% metal basis, C < 10 ppm, O = 160 ppm), Al (purity 99.5% metal basis), Y₂O₃ (purity 99.9%, total rare earth oxide 0.1% max.), Ti (purity 99.8% metal basis, C = 0.086%, O = 0.694%),

Table 1

Chemical composition of the FeCrAl-ODS initial powder mixtures as prepared for mechanical alloying.

Sample	Chemical composition [wt.%]					
	Fe	Cr	Al	Y_2O_3	Ti	v
ODS-1-Ti	Balance	12.0	5.0	0.3	1.0	-
ODS-2-TiV	Balance	12.0	5.0	0.3	1.0	0.5

and V (purity 99.5% metal basis, C \leq 0.034%, O \leq 0.035%). The initial particle size of powders was below 150 µm. The powders were mechanically alloyed in a high-energy Retsch PM100 planetary ball mill under an argon atmosphere. The preparation of the powders, such as weighting and closing the grinding jar hermetically before milling, was performed in a glove box under argon gas to minimize the powder oxidation effect during milling. The powders of a total weight of 50 g were inserted into the grinding jar for one milling cycle. The grinding jar and balls used in the process were made of martensitic stainless steel (X90CrMoV18). Balls (185 pieces) with a diameter of 7 mm were used in the mechanical alloying process, and the grinding jar volume was 125 ml. This gives a balls-to-powder ratio (BPR) of 5, and the free space in the grinding jar was about 70%. The milling was conducted for 50 h at 250 rotations per minute (rpm). Every 15 min, a break of 15 min was applied to cool down the powder and maintain the mechanical alloying process close to room temperature. After each interval, a change in the direction of rotation of the grinding jar was applied. Adding a process control agent (PCA), such as ethanol or stearic acid, could prevent the formation of agglomerates and excessive cold welding [41,42]. However, the PCA addition could contaminate powder, e.g., with carbon, oxygen, etc.; therefore, PCA was not added in this study [42]. In the next step, mechanically alloyed powders were sintered using the SPS technique in an apparatus of the Lukasiewicz Institute of Microelectronics and Photonics' own design. The SPS powder consolidation process was performed in a graphite round die with a diameter of 25 mm. The height of the samples was approximately 9 mm. The samples were heated at a rate of 100 °C/min to 900 °C, and then the heating rate was slowed down to 50 °C until the sintering temperature (1050 °C) was reached. The temperature of 1050 °C and uniaxial pressure of 40 MPa were kept for 10 min. After the holding time, the samples were cooled to room temperature with an average cooling rate of 10 °C/min. The external load was released from 40 to 0 MPa directly after the sintering time. The use of graphite dies and punches can affect the diffusion of carbon into the sintered material. However, due to the short exposure time of the material at elevated temperatures, the diffusion range is small. In order to avoid this effect in the tested material, the samples were ground after the sintering process, and the removed material thickness was 0.5 mm.

2.2. Experimental procedures

The studies to understand the chemical and microstructural homogeneity of the investigated samples were carried out using scanning electron microscopy (SEM), including scanning transmission mode (STEM), transmission electron microscopy (TEM), energy dispersive Xray spectroscopy (EDS) mapping, and electron backscatter diffraction (EBSD). The bulk samples were prepared for SEM observations and EBSD using a procedure that consists of mechanical polishing at a stepwise decreasing grain size of the polishing abrasive paper and electropolishing (60% perchloric acid 70 ml + ethanol 1000 ml, 50 s, 10 °C, 30 V) with Struers Lectropol system. The microstructural SEM observations were performed using ThermoFisher ScientificTM HeliosTM 5 UX Scanning Electron Microscope using Everhart Thornley Detector (ETD). The device is equipped with an EDAX Elite Super Detector, which was used for EDS. The electron energy used during the EDS mapping and analysis was in the range of 15 keV. The EBSD analyses were conducted by the EDAX Velocity Pro-EBSD system. The mapping of the specimens was done using a 20 kV electron beam of ~10 nA probe current. The

grain reconstruction in the collected EBSD maps has been performed by EDAX OIM Analysis 8 software. The lamellas for TEM and STEM were prepared using the focused ion beam (FIB) lift-out technique. Preliminary observations of the lamellas were carried out using STEM mode. More detailed analyses, including chemical composition analyses of precipitates, were conducted using TEMs: a JEOL JEM 1200EX II device operating at 120 kV and a JEOL JEM-F200 operating at 200 kV equipped with two EDS detectors. The volume fraction and size distribution of nanometric precipitates (<100 nm) were determined based on multiple STEM/TEM images using ImageJ software. The X-ray fluorescence (XRF) spectroscopy measurements were carried out on the EDX3600H energy dispersive spectrometer by Skyray Instruments. The excitation radiation came from an Rh lamp with a voltage of U = 40 kV and a current of $I = 200 \,\mu\text{A}$; the energy range from 4.2 keV to 40 keV was analyzed. In the spectrum, in addition to the excited lines of elements from the sample (Fe, Cr, Ti, Y, and V), there are also visible weak escape lines (the difference in the energy of the excited line and the excitation of the detector element - Si 1.74 keV), and the sum of the excited lines above all the visible sum from the strongest K_{α} Fe line. Carbon content measurements in bulk samples were performed using a CS-600 LECO analyzer. The analyses were carried out on thin slices (about 1 g) cut through the cross-section of the entire sample. Oxygen content measurements in bulk samples were carried out using a TCHEN600 LECO device. The analyses were performed on slices of materials (about 2 g) cut through the cross-section of the entire sample.

The phase analysis and crystal structure investigations of powder and bulk samples were carried out using the X-ray diffraction (XRD) technique. Diffraction patterns (DPs) acquisition was performed using a divergent X-Ray beam and the Bragg-Brentano parafocusing geometry at the Bruker D8 Advance diffractometer with θ/θ goniometer of a 280 mm radius. The X-Ray tube had a Cu anode and was powered by 40 kV and 40 mA. Data were acquired by the LYNXEYE XE-T detector working in the high energy resolution ($\Delta E < 380$ eV at 8 keV, energy window optimized for $Cu_{K\alpha}$ lines) and 1D modes without Ni-filter, and its matrix (192 strips, each 0.075 mm wide) covered 2.941° of 20. In the primary optics, the 0.4 mm fixed divergent slit, and 2.5° axial Soller slits were mounted, while the detector optics contained only 2.5° axial Soller slits. The measurement range covered 20 starting between 10° and 40° up until 145°. The Bruker DIFFRAC.EVA program with the database of diffraction standards ICDD PDF4+ 2022 [50] and DIFFRAC.TOPAS programs were used for phase analysis and to refine the models of the identified phases to satisfactorily describe the experimental diffraction patterns. The TOPAS program uses the fundamental parameters profile fitting (FPPF) approach to account for instrumental effects. In the case of powder samples Rietveld approach was used to optimize the model crystal structures' parameters (lattice constants, size- and strain broadening effect - following Davor Balzar double-Voigt function approach [51], sites occupancies, and the background profile). Diffraction peak intensities were calculated on the basis of the structure factor. In the case of bulk sintered samples, their contribution to the scattering was modeled using a set of PseudoVoigt analytical functions representing the $\text{Cu}_{K\alpha}$ lines in the X-ray tube spectrum per each diffraction peak. The Lorentzian to Gaussian ratio in the Voigt functions was refined and set common for all diffraction peaks. The 20 positions and FWHM values (full width at half maximum) of the Voigt functions were refined separately for each diffraction peak. The crystal lattice constant was obtained through the Nelson-Riley extrapolation [52]. The size-strain contribution to the FWHM was assessed using the Williamson-Hall approach [53]

The density of bulk samples was measured according to Archimedes' law. Consolidated sample discs were polished with SiC paper to remove surface contamination (approximately 0.5 mm) from the graphite die. The samples were weighed in air and distilled water at 23 °C using an analytical balance with an accuracy of 5 decimal places. The measured density was compared to the theoretical density estimated using the rule of mixtures based on the densities of pure constituent elements. The hardness of bulk samples was evaluated by Vickers microhardness measurements using an HV-1000 Huatec Group microhardness tester under a load of 4.90 N and a dwell time of 15 s. The Vickers microhardness values reported are the average values obtained from five measurements. Nanomechanical investigations were performed on a NanoTest Vantage System provided by Micro Materials Ltd. Nanoindentation measurements were carried out at room temperature with a Berkovich-shaped diamond indenter tip. Before the tests, the indenter's diamond area function (DAF) was calibrated using fused silica with known mechanical properties. Indentations were performed in singleforce mode by using 11 forces in the range from 0.5 mN to 10 mN. Each measurement was repeated at least 20 times with 20 µm spacing between the indents. Loading and unloading times for each experiment were set for 5 s and 3 s for loads of 0.5-4 mN and 10 s and 5 s for loads of 5-10 mN, respectively. Dwell time was set for 2 s. Nanomechanical properties were extracted from the load-displacement curves (L-D) by implementing Oliver and Pharr method [54].

3. Results

3.1. Mechanical alloying results

The SEM observations of mechanically alloyed powders show flattened particles of irregular shapes and rugged surfaces (Fig. 1). There are no significant changes in powder morphology between the two investigated chemical compositions. In both powders, large distribution of particle size is observed based on the SEM images. Small particles with a diameter of a few micrometers and big agglomerates of a size larger than 150 μ m can be noticed.

The SEM-EDS chemical composition point analyses (at least 15 points for each sample) of the powders, shown in Fig. 2, reveal the presence of all elements for a given composition in the mechanically alloyed powders. The results suggest that the milling parameters were chosen appropriately to obtain homogeneous powder particles after mechanical alloying. Moreover, no pure (non-alloyed) particles were found in milled powders. It is essential that no presence of isolated Y_2O_3 particles was found; therefore, it can be expected that the oxide particles are dispersed inside uniform grains and will be homogeneously distributed in the material after sintering.

The XRD results of pure powders before mechanical alloying are summarized in Table 2. The results for pure powders reveal single-phase diffraction patterns with lattice parameters corresponding to the standards from the ICDD database (Table 2). The crystallite size of these powders, which is the volume-weighted average size of the scattering domain, varies a lot from 25 nm Ti to 180 nm for Al, similar to the strain parameter. The XRD results of mechanically alloyed powders are presented in Fig. 3 and also summarized in Table 2.

The diffraction patterns of the powders after mechanical alloying show only the reflections characteristic of the bcc phases. Each diffraction peak can be deconvoluted into two scattering contributions. The dominant maxima contribution yielded peaks with lower FWHMs and positions close to the positions of the pure Fe phase (bcc1). Broader peaks lie at slightly lower angles, resulting in an apparent left-hand asymmetry of the experimental peaks. The positions of these broader peaks with smaller intensity are close to the pure Cr reflexes positions (bcc2). A model of two solid solution bcc phases (bcc1 and bcc2) was assumed for the analysis. In the ODS-1-Ti powder, the bcc1 phase is largely predominant over the bcc2, while in the ODS-2-TiV powder, the content of both phases is almost equal (Table 1). Therefore, it is very unlikely that only a small addition of vanadium could significantly influence the phase formation during mechanical alloying. The two bcc phases differ only in substitution and occupation of metal atoms in the crystal lattice, so their formation is somewhat random during milling. The crystallite size of the bcc1 phase is 23-25 nm, while the crystallite size of the bcc2 phase is either 7 or 14 nm depending on the sample. The results show a significant decrease in crystallite size during mechanical alloying. It is evident compared to the pure Fe powder with a crystallite size of 74 nm, and pure Cr domains had approximately 22 nm in diameter. The decrease in crystallite size is the effect of the disintegration of domains consisting of an array of high-density dislocations created during mechanical alloying [55].

3.2. Microstructure, phase analysis, and hardness of bulk samples

The density measurements, shown in Table 3, reveal a relative density of approximately 96% for both samples consolidated by SPS. Even though the relative density is quite low, it should be noted that theoretical density was determined using the rule of mixtures based on the density of pure metals and Y_2O_3 . During the processing, a significant amount of oxide precipitates formed (also from the oxygen, which comes as contamination), which can decrease density. Therefore, the relative density values should be considered rather as guidance enabling comparison between two samples than the value showing the porosity level.

SEM microstructural investigations confirm that the SPS consolidation at 1050 °C of the mechanically alloyed powder led to high-density bulk samples. The microstructure is composed mainly of different size α -ferrite micrometric grains of ca. 1 to 8 μ m, and many sub-micrometric grains (Figs. 4a,b and d,e). Apart from the ferrite grains, oxide particles and carbide precipitates of size up to 1 μ m and nanoprecipitates are also present in the matrix. The chains of precipitates are visible at grain boundaries. More chains of precipitates seem to be present in the ODS-2-



Fig. 1. SEM images of FeCrAl ODS powders after mechanical alloying: a) ODS-1-Ti, b) ODS-2-TiV.



Fig. 2. SEM-EDS chemical composition analysis of FeCrAl ODS powders after mechanical alloying: a) ODS-1-Ti, b) ODS-2-TiV.

 Table 2

 XRD results of pure and mechanically alloyed FeCrAl-ODS powders.

Powder	Structure	Space group	Lattice constant [Å]	Crystallite size [nm]	Strain parameter	Phase content [%]	PDF number
Fe	bcc	Im3m	2.866	74	0.0007	100	04-002-1253
Cr	bcc	Im3m	2.885	22	0.0031	100	04–004–8454
Al	fcc	Fm3m	4.049	180	0.0008	100	03-065-2869
Ti	hcp	P6 ₃ /mmc	a = 2.951	25	0.0010	100	03-065-3362
			c = 4.684				
V	bcc	Im3m	3.0335	34	0.0012	100	01-071-3955
Y_2O_3	cubic	Ia3	10.606	98	0.0005	100	04-009-8404
ODS-1-Ti	bcc1	Im3m	2.868	23	0.0047	87	_
	bcc2	Im3m	2.891	14	0.0057	13	_
ODS-2-TiV	bcc1	Im 3 m	2.865	25	0.0014	53	_
	bcc2	Im 3 m	2.885	7	0.0006	47	_

TiV sample (highlighted in Fig. 4e), which could be related to the vanadium's ability to form carbides. Moreover, some precipitates (visible as white dots) that seem to be fragmented are highlighted in the secondary images of Figs. 4c,f, and 5. The secondary electron images confirm that some pores (black dots) are present in bulk samples, which is common for materials prepared using powder metallurgy. However, porosity seems to be somewhat limited, and pores are homogeneously distributed.

The number of coarse precipitates and nanoparticles is well confirmed by SEM-EDS mapping results for Fe, Cr, Ti, V, Y, and O, shown in Figs. 5a and b. As shown in the SEM-EDS maps and already stated above, the chromium-rich ferrite (α -Fe(Cr)) phase is a predominant constituent in FeCrAl ODS steels. However, it is shown in the (Y-Ti-Al-O) atom map in Fig. 5 that Y, Ti, Al, O enriched nanoclusters are homogeneously dispersed in the FeCrAl ODS steels matrix. Qualitatively, Y, Ti, Al, and O enrichment areas coincided with Fe and Cr depletion areas. SEM-EDS maps show the presence of both the distinct (Y, Ti, O) – enriched and (Y, Al, O) – enriched clusters. The chemical composition measurements by SEM-EDS reveal the content of the main elements is close to their content in the initial powder mixture before mechanical alloying. Although the vanadium is not visible on the SEM-EDS maps, its presence in the ODS-2-TiV sample was confirmed qualitatively by XRF



Fig. 3. XRD patterns of mechanically alloyed powders – ODS-1-Ti and ODS-2-TiV.

spectroscopy. The comparison of the inserts in Fig. 6 clearly shows an increase of intensity around 5.0 keV, which corresponds both to the $K_{\alpha}V$ and $K_{\beta}Ti$ lines. The carbon content measurements in sintered samples reveal the carbon content of 0.030 wt.% in the ODS-1-Ti sample and 0.078 wt.% in the ODS-2-TiV sample. The carbon is the result of the contamination arising from different sources, i.e., contamination in commercially purchased powder, contamination during mechanical alloying from milling media (grinding jar and balls), and contamination from graphite die during SPS. The oxygen content measurements reveal the oxygen content of 0.44 wt.% in the ODS-1-Ti sample and 0.42 wt.% in the ODS-2-TiV sample. The results are somewhat similar in both samples; therefore, vanadium does not have a significant effect on oxygen contamination. It should be noted that the oxygen content is

 Table 3

 The density of FeCrAl-ODS samples after SPS.

significantly higher than the oxygen intentionally introduced via 0.3 wt. % addition of Y_2O_3 (approximately 0.064 wt.% oxygen introduced). The contamination by oxygen could occur during mechanical alloying (even though the grinding jar was closed under an argon atmosphere), during manipulation with powder in the glove box, or during spark plasma sintering even though it was conducted under argon. In addition, the raw elemental powders contain certain oxygen contamination (please refer to the "2.1. Mechanical alloying and consolidation process" section). Even though the oxygen content seems to be high, it is comparable to many other studies investigating ODS alloys with similar content of Y_2O_3 , e.g., 0.425 wt.% in the studies by Oksiuta et al. [16] or 0.4 wt.% in the investigations by Mori et al. [56].

The TEM and STEM-EDS studies were conducted to evaluate the presence of nanoprecipitates in the investigated materials. The low magnification TEM images (Fig. 7a) show the matrix grains of different sizes from a few hundred nanometers to a few micrometers. It is a perfect agreement with the SEM results (Fig. 4). The STEM results (Fig. 7b) show nanometric precipitates distributed inside the grains and at the grain boundaries. The volume fraction of nanometric precipitates is 1.87% for the ODS-1-Ti sample and 2.57% for the ODS-2-TiV sample. The coarser precipitates (>100 nm) were also found. One of the coarse precipitates, shown in Fig. 7c, was identified as Y₂O₃ based on selected area electron diffraction patterns (not shown here) and EDS analysis. The TEM images at higher magnification (Figs. 7c and d) reveal many nanometric precipitates. The histograms of nanoprecipitates (only precipitates of diameter <100 nm) size distribution show that most of the precipitates are in size between 15 and 50 nm in both samples. However, due to the small size of the particles, the selected area electron diffraction does not allow for clearly identifying the crystallographic structure of the precipitates.

The STEM-EDS results, shown in Fig. 8, reveal that most nanometric precipitates are significantly enriched in Al. Yttrium is more homogenously distributed in the investigated area, although there are some nanometric areas of a higher yttrium concentration that are matched with zones rich in aluminum and oxygen. It could indicate the formation

Sample	Theoretical density [g/cm ³]	Measured density [g/cm ³]	Relative density [%]
ODS-1-Ti	7.49	7.19	96.0
ODS-2-TiV	7.48	7.19	96.1



Fig. 4. SEM images of FeCrAl-ODS bulk samples microstructure: a) and b) backscattered electron image of ODS-1-Ti, c) secondary electron image of ODS-1-Ti, d) and e) backscattered electron image of ODS-2-TiV, f) secondary electron image of ODS-2-TiV.



Fig. 5. SEM-EDS mapping of the SPS bulk samples: a) ODS-1-Ti and b) ODS-2-TiV.

of complex oxides containing Y and Al. Nanometric zones rich only in yttrium and oxygen could also be spotted, which confirms the presence of non-dissolved Y_2O_3 oxides. Many nanometric zones enriched in titanium match those rich in carbon (especially visible in the ODS-1-Ti sample), suggesting Ti-rich carbides' formation. In the case of the ODS-2-TiV sample, nanometric zones rich in Ti match those rich in V. Some of these precipitates seem to be rich in carbon and others in oxygen, which hints at the formation of carbide and oxides with these elements. Therefore, it shows that Ti and V participate in the formation of precipitates.

The EBSD observations, shown in Fig. 9, reveal that apart from large α -ferrite grains 1–8 μ m, some areas within the FeCrAl ODS material where very fine submicron size α -ferrite grains are also present. The EBSD inverse pole figure maps and histograms of grain size indicate that the SPS consolidation of FeCrAl-based ODS steels MA powders at 1050 °C has resulted in randomly oriented grains and bimodal grain size distribution. Such a bimodal grain size distribution is a typical feature observed in ODS steels sintered by this method. The ODS-2-TiV sample presents a smaller average grain size than the ODS-1-Ti sample, which shows that the addition of vanadium affects grain refining grain size (Fig. 9c).

The XRD results, shown in Fig. 10, acquired from the electropolished cross sections of the bulk samples indicate large similarities between the ODS-1-Ti and ODS-2-TiV specimens. The bcc lattice constants obtained via the Nelson-Riley extrapolation are similar, approximately 2.885 Å. The individual fitting of each peak was required due to anisotropy of the peaks broadening observed for the 2 0 0 and 3 1 0 peaks with respect to the others. These peaks represent planes that are inclined at 18.43° to each other, so at a relatively small angle. Thus, these peaks are affected by the crystal structure properties likewise. In the case of both materials,

the slopes of the line fit to the points corresponding to the 2 0 0 and 3 1 0 peaks and to the others qualitatively identical, so the broadening of these peaks reflects the smaller size of crystallites in the [100] direction. However, no texture nor residual stress is observed in the bulk samples. The parameters describing the crystal lattice of the sintered ODS-1-Ti and ODS-2-TiV samples are given in Table 4. The traces of other phases were too weak to allow their structural analysis or even confirm their presence judging by the XRD patterns.

The hardness of ODS-1-Ti is 286 ± 7 HV, while the hardness of ODS-2-TiV is 320±11 HV. Therefore, sample ODS-2-TiV shows higher hardness (about 10% higher) than sample ODS-1-Ti. The volume fraction of nanometric precipitates (<100 nm) is higher in ODS-2-TiV (2.57%) compared to the ODS-1-Ti sample (1.87%), which could have an important effect on hardness. The higher hardness of the ODS-2-TiV sample could be the effect of 0.5 wt.% of vanadium addition in ODS-2-TiV, which is considered as an eminent element for strong and easy controllable precipitation strengthening, mainly by carbides forming. The presence of vanadium-rich precipitates was confirmed by STEM-EDS (shown in Fig. 8b). The hardness of sintered samples is comparable to some other FeCrAl ODS alloys, e.g., the alloy prepared using MA and HIP by Chen and Dong [41] shows the hardness of 305 HV or the alloy 7 wt.% of Al fabricated using MA and HE by Sang et al. [57] reveals the hardness of approximately 325 GPa. Nevertheless, it should be noted that there are articles about FeCrAl ODS alloys consolidated by SPS (e.g., [58,59]) showing higher hardness than those obtained in this study. The nanoindentation tests were performed to better characterize the mechanical properties of the produced sample before heat treatments and irradiation experiments planned later in the project. The results are shown in Figs. 11a and b. The SEM images of the indention sites after the test under a 10 mN load are presented in Figs. 11c and d. One can



Fig. 6. XRF spectrum measurements: a) ODS-1-Ti and b) ODS-2-TiV.

observe that initially, the recorded hardness value decreases to be stabilized around 200 nm depth. This effect is related to the sample roughness and proper contact of the indenter tip with the material. Above 200 nm of contact depth, the recorded hardness value seems to stabilize, which indicates that we have a fully developed plastic zone under the indenter tip. These values should be treated as true hardness values. A similar situation occurs for reduced Young's modulus values. The hardness at the highest contact depth (> 250 nm) is 3.78 ± 0.34 GPa (converted to HV, it is 350±31 HV) for ODS-1-Ti and 4.83±0.43 GPa (448±39 HV) for ODS-2-TiV. Both values are higher than the microhardness measured under the load of 4.90 N, probably due to the higher indentation size effect (ISE) for the lower loads. However, it confirms the observation that the sample with the addition of V present higher hardness. It is related to the more pronounced formation of reinforcing oxide and carbide precipitates (higher volume fraction of nanometric precipitates in the sample with the addition of V confirmed by TEM-EDS studies) and solid solution strengthening. The sample with the addition of V also shows a higher reduced Young's modulus.

4. Discussion

4.1. Mechanical alloying

The observed rugged surface morphology of the mechanically alloyed powders confirms the plastic deformation of powder during mechanical alloying, which is necessary in solid state processing to form

the alloyed powder. The large particle size distribution and the presence of agglomerates (>50 µm) were also found in other studies of ODS alloys produced by mechanical alloying [6]. The successful mechanical alloying was confirmed by XRD by the detection of two bcc phases. It is not surprising that bcc1 (with lattice parameter close to Fe) and bcc2 (with lattice parameter close to Cr) phases form during mechanical alloying because Fe is a base element, while Cr is dominating alloving element. The two-phase structure suggests that the mechanical alloving did not completely homogenize the powder; although both bcc phases seem very close regarding the lattice parameter, the differences are almost not significant between them. The consolidation by SPS would lead to complete homogenization - the formation of a single bcc phase matrix. A longer milling time and higher ball-to-powder ratio could possibly further increase homogeneity (formation of a single bcc phase); however, it would undoubtedly decrease the process's economic aspect, which is essential to transfer the production process to industrial conditions. A higher rotation speed (>250 rpm) during milling could increase homogeneity. However, it could lead to the sticking of powder particles to the walls of the grinding jar and thus reducing the amount of recuperated powder after the process.

4.2. Microstructure, phase analysis, and hardness of bulk samples

The benefit of using the SPS technique is to achieve a high density of material in a relatively shorter time than the HP or HIP technique, and thus to limit grain growth after the sintering process [40,47]. Moreover, in opposition to HIP, when consolidating metal powder with SPS, some other effects may play a dominant role in the densification process. These are mass transport at both micro and macro levels, electro-migration, and generation of highly defected structures with point defects [60].

The existence of different types (highlighted in secondary electron images in Figs. 4 and 5) of cuboidal and almost spherical oxide particles may relate to regions of enhanced Joule heating in the rapidly consolidating powder mass during SPS, which promotes their fragmentation in the matrix. Based on the SEM-EDS analyses, the Y-Ti-O oxide clusters seem to be more homogeneously dispersed in the matrix, while the Y-Al-O appear to be finer than the Y-Ti-O particles. STEM-EDS results of nanometric precipitates show that many of them are significantly enriched in aluminum, oxygen, and probably in yttrium, which suggests the formation of fine Y-Al-O oxides in agreement with SEM-EDS. SEM-EDS maps also clearly revealed the Al₂O₃ particles, which indeed had a significantly high content of Al and O. Based on the literature data, Al addition in the range of 2-6% can dramatically improve the corrosion resistance, including corrosion in liquid metals and oxidation resistance of FeCrAl-based ODS steels, which is essential for solving issues in the design of Generation IV nuclear reactors [9,10,36,61]. However, Al addition is known to decrease the high-temperature strength in these ODS steels due to the formation of coarse $Y_4Al_2O_9$ (known as YAM), Y₃Al₅O₁₂ (known as YAG), and Al₂O₃ particles [6,9,28,36,62]. It also has an effect on thermal aging embrittlement associated with high Cr (>12%) containing ferritic alloys, as mentioned in literature [7,8], which the authors want to investigate in later experiments related to the heat treatment and aging processes of the tested ODS steels. The nano-sized carbides and oxides, which volume fraction is 1.87% in the ODS-1-Ti sample and 2.57% in the ODS-2-TiV sample, can hinder grain boundary migration, inhibiting ODS steel's grain growth during operation in creep and radiation conditions [28,63]. The higher volume fraction of nanoprecipitates in the vanadium-containing sample could be due to the high affinity of vanadium to carbon and, thus, the formation of carbide precipitates. The STEM-EDS results confirm that vanadium and titanium participate in the formation of nanometric oxide and carbide precipitates. It should be noted that the formation of nanometric precipitates is preferable compared to micrometric precipitates to increase mechanical properties and irradiation resistance. In turn, the oxide precipitates in the investigated FeCrAl ODS steels could



Fig. 7. Transmission electron microscopy investigation of FeCrAl-ODS bulk samples: a) TEM low magnification bright field image of ODS-1-Ti sample, b) STEM image of ODS-2-TiV (yellow arrows indicated precipitates on grain boundaries, while red arrows point to intra-granular precipitates), c) TEM bright field image showing trans-granular and intra-granular precipitates in ODS-2-TiV sample, d) magnified TEM bright field image with the indicated size of selected precipitates in ODS-2-TiV sample, e) histogram of nanoprecipiates (<100 nm) size distribution in ODS-1-Ti sample, f) histogram of nanoprecipiates (<100 nm) size distribution in ODS-2-TiV sample.

be matched to Y_2O_3 (shown in Figs. 7c and 8) and probably Y-Al-O rich oxides. Due to the difference of oxygen to solute atoms affinity of different elements, the internal oxidation reaction can occur during MA and high-temperature consolidation of the ODS steel [23,59]. Considering such an effect, some Y_2O_3 nanoparticles in ODS-1-Ti and ODS-2-TiV samples can also combine with Al to form $Y_4Al_2O_9$ (e.g., [23]) and $Y_3Al_5O_{12}$ (e.g., [64]) complex oxides and stable Al_2O_3 oxide (e.g., [59]).

The bimodal distribution of grain size, revealed by EBSD, is essentially the result of a non-uniform strain distribution of the grains during the mechanical alloying process, as observed by other researchers [37, 47]. Moreover, such a microstructure is also attributed to effects associated with the formation of larger ferrite grains through grain growth in regions of lower nanoparticle density and inhomogeneity in their initial distribution, as well as a recrystallization process during sintering that does not fully occur (due to inhomogeneous temperature gradient [26]), in which large grains trap neighboring smaller higher energy state grains. The EBSD images indicate a random orientation of bcc grains, meaning that the samples should reveal isotropic properties. It is common for samples consolidated using SPS from mechanically alloyed powders [26,37,40,47,59].

The hardness and nanoindentation measurements reveal that adding vanadium causes the hardness to increase. As mentioned, vanadium is an eminent element for strong precipitation strengthening by forming

Fig. 8. STEM-EDS chemical composition analyses of nanometric precipitates: a) ODS-1-Ti, b) ODS-2-TiV.

Fig. 9. EBSD results of FeCrAl-ODS bulk samples: a) inverse pole figure map of ODS-1-Ti, b) inverse pole figure map of ODS-2-TiV, c) grain size distribution in ODS-1-Ti and ODS-2-TiV.

stable carbides during processing, even when present at relatively small levels (investigated FeCrAl ODS 0.5 wt.%). The addition of vanadium element to bcc ODS alloys could refine grain size by forming nanometric precipitates, which can pin grain boundaries and therefore limit grain growth during sintering. The smaller grain size in the ODS-2-TiV sample

compared to the ODS-1-Ti sample could be the effect of such a phenomenon. Moreover, nanoprecipitates could improve the material's properties during operation at elevated temperatures. The addition of V can also promote the formation of high-density, complex oxide nanoparticles [17]. The volume fraction of nanometric precipitate is higher in

Fig. 10. XRD patterns of FeCrAl-ODS bulk samples (a) ODS-1-Ti, (b) ODS-2-TiV.

the sample with the addition of V (2.57%) compared to the V-free sample (1.87%), which might confirm the positive impact of vanadium on the nanoprecipitates formation. It was confirmed by STEM-EDS analyses showing nanometric vanadium-rich precipitates. The presence of these nanoprecipitates and the large density of grain boundaries will

block the dislocations during plastic deformation, increasing the recorded hardness value. Moreover, the results of nanoindentation suggest that to understand the hardening effect caused by ion irradiation; one should probe material at least 150 nm depth (to obtain true mechanical properties). This means that the energy of heavy ions (e.g., Fe) should be of several MeV (to develop a sufficiently thick irradiation layer that will ensure data collection without the impact of the unmodified bulk of the material). Therefore, these data helped to prepare appropriate irradiation experiments in the project's next step.

4.3. Future directions

Our further experiments will be focused on heat treatments of ODS samples, such as the normalizing and tempering process, and on high-temperature corrosion tests to check the α' formation embrittlement of the steels and the effect of Al, Ti, and V addition to FeCrAl-ODS alloys whose contents enhance the structure stability, mechanical properties, and as well corrosion and oxidation properties. Thermal properties of these materials will also be tested to find an accurate balance between Fe, Cr, and Al and other elements to maximize possibilities of the ODS material safe operation in IV Generation Reactors. The campaign of mechanical tests using miniaturized samples such as tensile tests at room temperature, tensile tests at elevated temperatures close to the operating

Table 4

XRD results of the sintered ODS-1-Ti and ODS-2-TiV samples. Crystallites above 200 nm in diameter yield negligible peak broadening comparing to the given lattice strain.

Sample	Lattice constant [Å]	Strain parameter ε_0	Crystallite size in different crystallographic directions [nm]	
			[110], [211], [220], [222]	[200], [310]
ODS-1-Ti ODS-2-TiV	2.8848 2.8849	0.00038 0.00033	>200 >200	140 140

Fig. 11. Top surface nanoindentation results: a) hardness vs. contact depth, b) reduced Young's modulus vs. contact depth, d) SEM image of indented made under the load of 10 mN in ODS-1-Ti, d) SEM image of indented made under the load of 10 mN in ODS-2-TiV.

conditions in Generation IV nuclear reactor (e.g., 700 $^{\circ}$ C), and Charpy impact test will be carried out to fully characterize the studied materials. Finally, the ion implantation experiments will be conducted to evaluate the irradiation resistance of these alloys.

5. Conclusions

The ODS FeCrAl-Y₂O₃ steels with different additions of Ti and V were successfully prepared by powder metallurgy. The mechanically alloyed powder presents two bcc solid solution phases with similar lattice parameters. The results show a significant decrease in crystallite size from 74 nm (Fe pure powder) to approximately 25 nm during mechanical alloying. The SPS consolidated samples show good densification and α -ferrite fine microstructure with most grains of about 1 μ m. The sample with the addition of V shows a slightly smaller grain size and a higher volume fraction of nanoprecipitates, including vanadium-rich precipitates, which reveals the positive effect of this element on the microstructure. In both investigated materials, many nano-size (15-50 nm) and coarser (up to 1 µm) oxide and carbide precipitates are formed. The nano-sized particles increase the mechanical properties of the alloys and should increase the irradiation resistance by being the sinks for defects. The sample with the addition of V shows a higher hardness (4.83 ± 0.43 GPa vs. 3.78 ± 0.34 GPa), which suggests the positive role of V in the formation of reinforcing nano-sized particles. The presence of vanadium-rich precipitates was confirmed by STEM-EDS. Moreover, the nanoindentation indicates that the material should be probed at least 150 nm depth to understand and measure the hardening caused by ion irradiation.

CRediT authorship contribution statement

Jaroslaw J. Jasinski: Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing. Tomasz Stasiak: Formal analysis, Visualization, Writing – original draft. Wojciech Chmurzynski: Investigation, Formal analysis, Writing – original draft. Lukasz Kurpaska: Conceptualization, Methodology, Formal analysis, Writing – review & editing, Funding acquisition. Marcin Chmielewski: Investigation. Malgorzata Frelek-Kozak: Investigation, Formal analysis, Writing – review & editing. Magdalena Wilczopolska: Investigation, Formal analysis. Katarzyna Mulewska: Investigation, Formal analysis, Maciej Zielinski: Investigation, Formal analysis, Writing – original draft, Writing – review & editing. Marcin Kowal: Investigation, Formal analysis. Ryszard Diduszko: Investigation, Formal analysis. Witold Chrominski: Investigation. Jacek Jagielski: Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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