Development of ceramic dispersion strengthened 316L steel composites

Ph. D. Thesis booklet

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1. Literature review and motivation

316L based oxide dispersion strengthened steels have attracted attention for advanced nuclear applications such as fast and fusion reactors as other commercially available materials. These materials can be used in harsh environments at high neutron doses and elevated temperatures. Japan, Europe and the United States have developed this steel material for fusion and fourth generation nuclear reactors applications as well. Novel designs for future generation fusion reactors have demanding requirements for the structural materials. A new class of oxide dispersion strengthened steel (ODS) materials which are currently being developed have a high chance of meeting these requirements. Nanostructured ferritic, martensitic or austenitic ODS alloys are ideal candidates for high temperature applications such as high temperature heat exchangers or nuclear power plants.

The production of 316L based ODS involves many technological processes. The powder mixing, mechanical alloying, degassing, canning, hot extrusion, and heat treatments are the most used technological methods. It was shown that powder metallurgy process helped the dispersion of the big oxide agglomerations during conventional casting processes.

The aim of my PhD work was to realize novel ceramic dispersion strengthened steels and study of the effect of milling and sintering parameters. In the same time the impact of the different submicron sized ceramics (Si_3N_4, SiC, Y_2O_3) addition to the structural, mechanical and tribological properties of final 316L based composites prepared by attrition milling and spark plasma sintering has been investigated. These results demonstrated that the small amount of ceramic addition have significant influence on the final properties of composites and open the new routes for various novel applications.

2. Experimental Methods

2.1. Milling process

I used the commercial 316L stainless steel powder (Höganäs company) and various ceramic additions for novel CDS composite development. The submicron sized α- Si_3N_4 (UBE), the grade “C” Y_2O_3 and the SiC (H.C. Starck) were used for the powder mixtures. The high efficient attritor mill (01-HD/HDDM, Union Process) has been used for efficient dispersion of submicron sized ceramic powders (SiC, Si_3N_4, Y_2O_3) in 316L steel matrix. A stainless steel setup (jar, crossbar agitator, 3 mm diameter milling balls) has been used in order to minimize the powder contamination. The milling was performed at 600 rpm in ethanol for 5 h for grain size reduction and homogenization of powder mixtures (316L, non-oxide and oxide ceramic addition). The powders have been dried at 70°C, sieved for particles separation and stored well concealed boxes in order to avoid oxidation.

2.2. Sintering process

The spark plasma sintering process was performed in collaboration with the Department of Metallurgical and Materials Engineering, Istanbul Technical University in Turkey. SPS (Sinter-SPS-7.40MK-VII) was used for sintering of the milled powders at 900°C under 50 MPa mechanical pressure for 5 minutes dwelling time in vacuum. Sintered solid disks with ~ 100 mm diameter and ~ 9 mm thickness have been obtained.

2.3. Experimental techniques

The Archimedes method was used for the density measurements. Structure of reference and CDS composites was characterized by transmission electron microscopy (TEM Philips CM20, 200kV). Morphology of milled powder mixtures and sintered CDS composites was studied by scanning electron microscopy (SEM, LEO 1540 XB). Elemental analysis was measured by Röntec Si(Li) EDS detector situated in SEM. Phase analysis was carried out by the X-ray diffractometry (XRD) using a Bruker AXS D8 Discover diffractometer equipped with Göbel-mirror and a scintillation detector with Cu Ka radiation. The mechanical properties of novel composites were investigated. The hardness equipment (LEITZ WETZLAR GERMANY model 721 464) by Vickers diamond pyramid tip was used for determination of microhardness of reference and composites. The 3-point bending test has been performed using the INSTRON 2500 equipped with a special 3 points bending test setup. The tribology test has been performed at room temperature using a CSM+ HT Tribometer in dry conditions (no lubricant). A 5mm Si_3N_4 balls have been used as counterpart during the test. 5N normal load was applied on the Si_3N_4 ball against the sample surface with 1mm shift from the rotation axis. The international standards were applied for various mechanical tests.

3. Results

3.1. Structural properties of novel composites

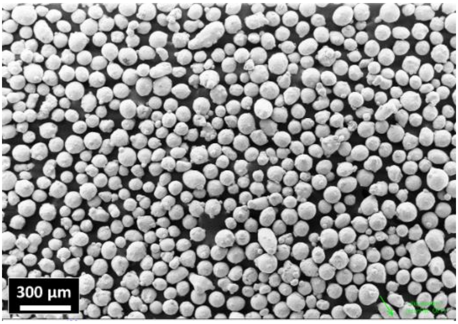
The preparation, mainly the milling process has significant effect to the structure of the composites. The morphological changes were observed after 5 hours high efficient milling in all types of novel CDS composites (Fig. 3.1). The reference sample consisted of 70 µm globular particles (Fig. 3.1a). During the milling process, the globular shaped-starting powders are plastically deformed/flattened into a very thin flake like shape grains (Fig. 3.1b). These thin flake like shape grains are after that broken into smaller particles. As a result of the flattening behavior the average grain size increased. The type (SiC, Si_3N_4, Y_2O_3) and amount (0.33wt%, 1 wt%) had influence on milling process and structure of final composite.

I estimated the milling efficiency by the ratio of the thin flake-like shape grains to the globular and the flattened grains. The addition of 0.33 wt% SiC (Fig

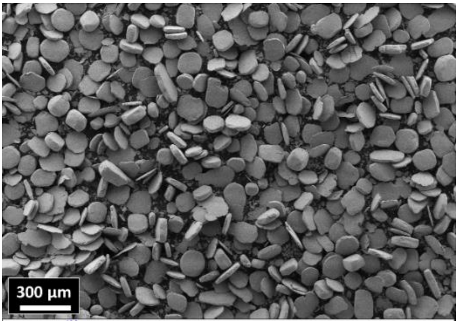
3.1c), 1wt% SiC (Fig 3.1d) or 0.33 Si_3N_4 (Fig 3.1e) showed the best milling efficiency results among the prepared composites (this is in comparison with the 316L milled powder). Followed by 0.33 wt% Y_2O_3 and 1 wt% Y_2O_3 addition. In the case of the 1 wt% Si_3N_4 addition there was no improvement of the milling efficiency comparing to the milled 316L steel powders.
The difference in the milling efficiency was mainly related to the following:

- The physical properties of the added particles. The density, hardness, size and morphology of the particles, these properties control the velocity, the dispersion of the added particles (top/middle/bottom of the milling jar) and the interaction with the steel grains under the impact forces.
- The chemical properties of the added particles, mainly the reactivity with ethanol and the 316L SS which influence directly the viscosity of the mixture and as the results the milling efficiency.
- The added ceramic particles are embedded in the surface of the steel grains under the strong impact forces which increases the hardness of the grain's surfaces, this last means that higher impact forces are transferred to the grain's cores. The plastic deformability of the grains increases significantly.

The structural observation of the sintered composites showed the nanosized ceramic particles distributed along the grain boundaries in all cases (Fig. 3.2) except in the case of the 316L/1 wt% Y_2O_3 where the yttria particles are agglomerated together (Fig 3.3f).



a)



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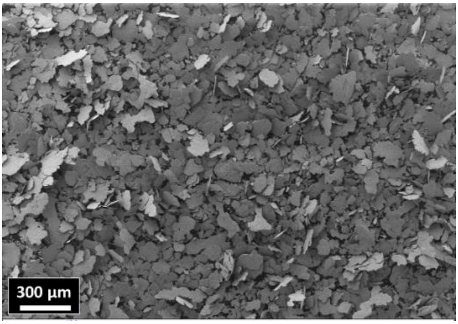
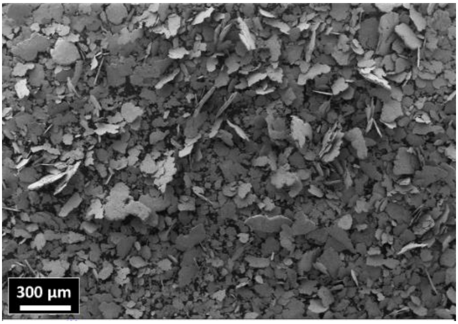


c)



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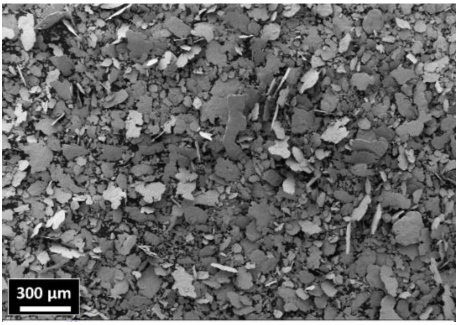
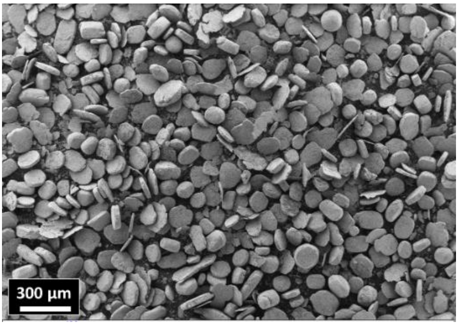


e)



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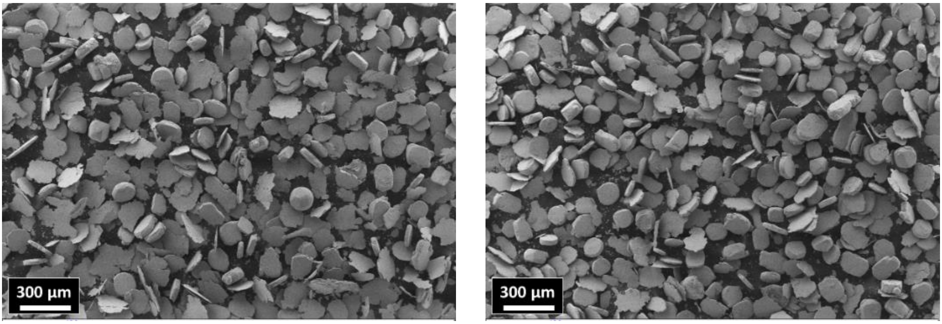
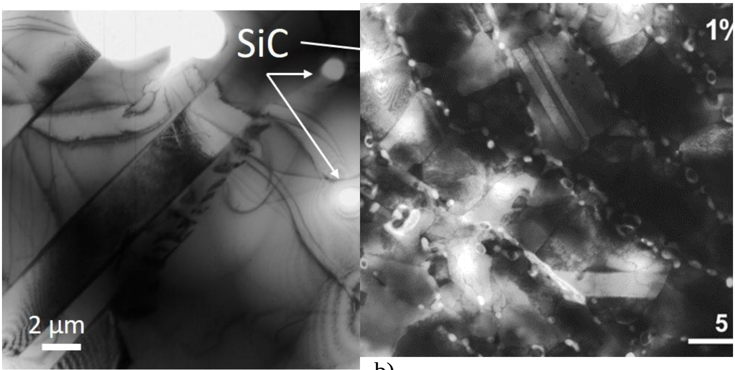
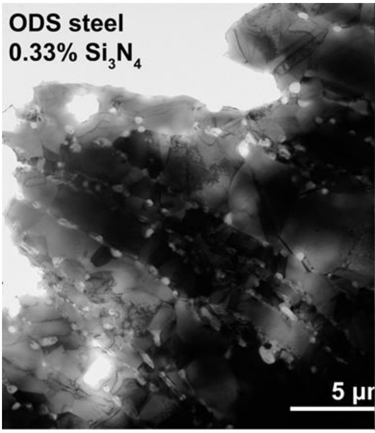


g) h)

Fig. 3.1. *Comparison of the morphology of milled powder mixtures and reference. a) 316L starting powder, b) milled 316L powder, c) milled 316L/0.33 wt% SiC, d) milled 316L/1 wt% SiC, e) milled 316L/0.33 wt%* Si_3N_4, *f) milled 316L/1 wt%* Si_3N_4, *g) milled 316L/0.33 wt%* Y_2O_3, *h) milled 316L/1 wt%* Y_2O_3.



a) b)



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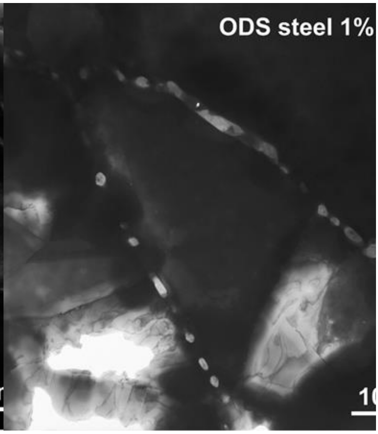

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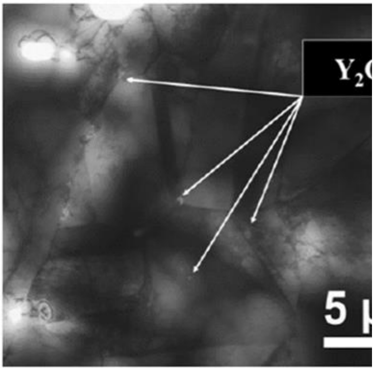

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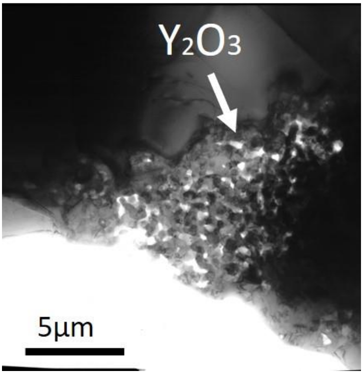

f)

Fig 3.2. *TEM images of the sintered composites. a) 316L/ 0.33 wt% SiC. b) 316L/1 wt% SiC, c) 316L/0.33 wt%* Si_3N_4*, d) 316L/1 wt%* Si_3N_4*, e) 316L/0.33 wt%* Y_2O_3*, f) 316L/1 wt%* Y_2O_3*.*

3.2. Mechanical properties of CDS composites

The most important property of the novel CDS sintered composites is the mechanical property (Fig. 6.3). The main focus of my PhD work was the enhance of hardness and bending strength of CDS composites compare to the 316L reference.

The milled and sintered reference 316L showed the highest density values and the lowest microhardness value ~ 1.75 GPa. The 0.33 wt% Si_3N_4 content caused the highest microhardness ~ 3.34 GPa. The very similar property was obtained by 0.33 wt% SiC addition with microhardness ~ 2.98 GPa. The 1 wt% SiC, Si_3N_4 and Y_2O_3 addition resulted the lower highest, but 2 times higher than reference 316L; 2.79 GPa and 2.69 GPa respectively.

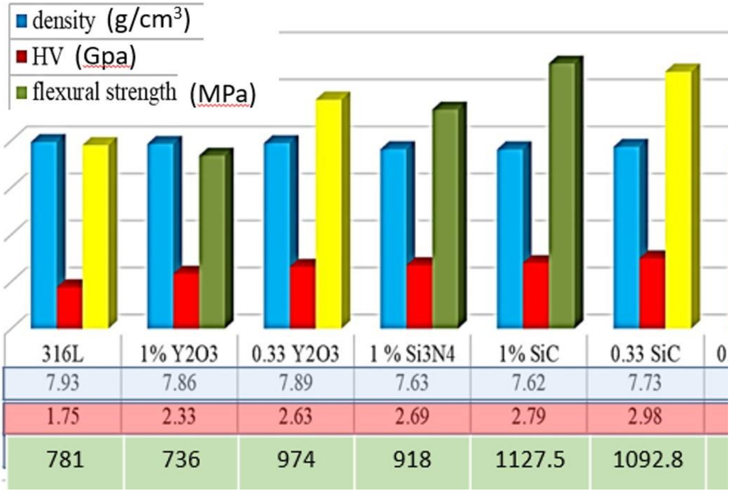

Fig. 3.3. *Mechanical properties comparison. The yellow bars in the chart means that the samples were not broken during the 3-point bending test.*

The 0.33 wt% Si_3N_4 and SiC non oxide ceramic addition provided the best mechanical properties with the highest microhardness and flexural strength values. This was a result of two main factors:

- the complex grain boundaries formed by the thin flake-like shape grains and the smaller broken particles.
- the presence and the homogeneous distribution of the ceramic additives in the grain boundaries which increases the deformability resistance by blocking/slowing down the movement of dislocations and grain boundaries during the deformation process.

The employing the nanosized ceramic additions provides better mechanical properties at room temperature comparing to the composites with nanosized ceramic oxides, which is more promising for applications at high temperatures.

4. Thesis Points

1. **I showed that the combined attrition milling and the spark plasma sintering are promising methods for the novel ceramic dispersed stainless steel composites (CDS) preparation.** The wet attrition milling depending on ceramic content provided homogeneous distribution of the ceramic additives (Si_3N_4, SiC, Y_2O_3) in the steel 316L matrix and imposed significant morphological transformation. The short time consolidation by spark plasma sintering prevented the excessive grains growth and maintained the homogeneous distribution of the additives **[S1, S2, S3, S4, S5, S6].**

2. **I showed that the employment of well dispersed small amounts** (0.33 and 1 wt%) of the **nanosized SiC particles in the 316L SS matrix improves its mechanical properties significantly.** The nanosized SiC particles embedded in the 316L SS grains and covering them homogeneously which increased its surface hardness and improved the milling efficiency resulting in a total morphological transformation of the starting globular shaped grains into larger and thin flake-like shape grains. The flake-like shape grains created complex grain boundaries during the sintering process and controlled the fracturing behavior. **[S5]**
3. **I showed that the Si_3N_4 amount had significant influence on the milling efficiency resulting in grains with different sizes and shapes.** The addition of 0.33 wt% Si_3N_4 gives better milling efficiency results comparing to the 1 wt% Si_3N_4 addition. The intensive milling assured an optimal coverage of 316L stainless steel grains with Si_3N_4 submicrometer sized particles in both cases which in turn resulted in improved mechanical properties (higher hardness, strength, lower friction coefficient) compared to reference sample. **[S2, S3, S7].**
4. **I proved that the addition of Y_2O_3 nanosized particles improved tribological properties of the 316L SS.** The addition of yttria nanosized particles reduce the wear rate of the 316L significantly. **[S6]**
5. **I proved that the CDS composites with nanosized ceramic particles (SiC and Si_3N_4) resulted better mechanical properties compared to the nanosized ceramic oxide particles (Y_2O_3).** The CDS composites are showing higher microhardness and higher flexural strength due to their more complex induced microstructures and more efficient distribution to the grain boundaries of the matrix **[S2, S3, S4, S5, S6].**

6. Publication activity

6.1. Publications

[S1] H.R. Ben Zine, A. Horváth, K. Balázsi, C. Balázsi, Submicron sized sintered ODS steels prepared by high efficient attritor milling and spark plasma sintering, *Courrier Du Savoir* 24 (2017) 93-100.

[S2] H.R. Ben Zine, F. C. Sahin, Zs. E. Horváth, Zs. Czigány, Á. Horváth, K. Balázsi, C. Balázsi, Effect of Si_3N_4 addition on the morphological and structural properties of the 316L stainless steel for nuclear applications, *Resolution and Discovery* 2 (2017) 23-30.

[S3] H.R. Ben Zine, K. Balázsi, C. Balázsi, Effect of the α-Si_3N_4 addition on the tribological properties of 316L stainless steel prepared by attrition milling and spark plasma sintering, *Anyagok Világa (Materials World)* 1 (2018) 9-16.

[S4] H.R. Ben Zine, C. Balázsi, K. Balázsi, Study of the different ceramic additions effect on the 316L morphological properties during attrition milling , *Anyagok Világa (Materials World)* 1 (2018) 36-43.

[S5] H. R. Ben Zine, F. C. Sahin, Zs. Czigány, K. Balázsi, C. Balázsi, Novel SiC dispersion strengthened austenitic steels prepared by powder technology, *Archives of Metallurgy and Materials, (2019) accepted for publication* ***IF 0.7***

[S6] H. R. Ben Zine, K. Balázsi, C. Balázsi, The effect of the chemical composition to the end-properties of ceramic dispersed strengthened 316L/Y_2O_3 composites, *Periodica Polytechnica Chemical Engineering* 63 : 3 (2019) 370-377 ***IF 1.382***

[S7] C. Balázsi, H. R. Ben Zine, M. Furko, Z. Czigány, L. Almásy, V. Ryukhtin, H. Murakami, G. Göller, O. Yucel, F.C. Sahin, K. Balázsi, S. Kobayashi, A. Horváth, Microstructural and magnetic characteristics of ceramic dispersion strengthened sintered stainless steels after thermal ageing, *Fusion Engineering and Design* 145 (2019) 46-53 ***IF 1.437***

6.2. Oral presentations

H.R. Ben Zine, C. Balázsi, K. Balázsi, A. Horváth, **Sixieme ecole sur les techniques de caracterisation des materiaux,** Biskra University12-13 March 2016, Algeria.

H.R. Ben Zine, C. Balázsi, K. Balázsi, A. Horváth, Development of nanostructured ODS steels by powder technology, **NEA International Workshop on Structural Materials for Innovative Nuclear Systems**, 11-14 July 2016, Manchester, UK.

H. R. Ben Zine, Zs. Cigány, F. S. Cinar, A. Horváth, K. Balázsi, C. Balázsi, The first seminar on "thin films and their applications" at Mohamed Khider University, 16 April 2017, Biskra, Algeria.

H. R. Ben Zine, Zs. Cigány, F. S. Cinar, A. Horváth, K. Balázsi, C. Balázsi, Si_3N_4 dispersion strengthened 316L stainless steels: structural and mechanical properties, **International Conference Deformation and Fracture in PM Materials**, 22 – 25 October 2017, High Tatras, Slovakia.

H.R. Ben Zine, F.S. Cinar, O. Yucel, K. Balázsi, A. Horváth, C. Balázsi, Preparation and Investigation of Boron Nitride Dispersion Strengthened Steels, **14th International Symposium on Novel and Nano Materials,** 3-8 July 2016, Budapest, Hungary.

H. R. Ben Zine, Zs. Cigány, F. S. Cinar, A. Horváth, K. Balázsi, C. Balázsi, 316L austenitic steel preparation with ceramic addition, **MMT2017,** 13 May 2017, Siófok, Hungary.

H. R. Ben Zine, Zs. Cigány, F. S. Cinar, Á. Horváth, K. Balázsi, C. Balázsi, Study of Si_3N_4 addition effect on structural and mechanical properties of the 316l stainless steel, **17thPhD Students Materials Science Day",** 4 December 2017, Pannon University, Veszprém, Hungary.

H. R. Ben Zine, Zs. Cigány, F. S. Cinar, A. Horváth, K. Balázsi, C. Balázsi , Preparation and characterization of ODS steels, **"Fine ceramics day" event of Hungarian Scientific Society of Silicate Industry,** 9 April 2018, MTA EK, Budapest, Hungary.

H. R. Ben Zine, K. Balázsi, C. Balázsi, Investigation of silicon carbide dispersion strengthened austenitic steels, FEMS Junior Euromat, 08-12 July 2018, Budapest, Hungary.

H. R. Ben Zine, K. Balázsi, C. Balázsi, Investigation of ceramic particle dispersion strengthened austenitic steel, **2nd "Fine ceramics day" event of Hungarian Scientific Society of Silicate Industry,** 19/03/2019, Budapest, Hungary.

6.3.Posters

H.R. Ben Zine, C. Balázsi, K. Balázsi, A. Horváth, Development of nanostructured ODS steels by powder technology, **NEA International Workshop on Structural Materials for Innovative Nuclear Systems**, 11-14 July 2016, Manchester, UK.

H. R. Ben Zine, Zs. Cigány, F. S. Cinar, A. Horváth, K. Balázsi, C. Balázsi, Effect of ceramic addition on structural and mechanical properties of steel alloys. ECERS 2017, Budapest, Hungary.

7. Scientific Parameters

All Publications: 7	Publications related to Ph.D work: 7
Cumulative impact Factor: 3.519	Impact factors related to PhD work: 3.519
All Citations: 1	Citations related to Ph.D work: 1