

## PREPARATION OF FERRITIC 17%Cr ODS STEEL BY MECHANICAL ALLOYING FROM PREALLOYED STEEL POWDER

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### **Abstract**

*The paper describes preparation of 17Cr-1Mo-Y<sub>2</sub>O<sub>3</sub> ODS steel by means of mechanical alloying. The composite powder was prepared from commercially available AISI 434LHC steel powder by adding 0.25 wt.% of metallic yttrium or by adding 0.25 wt.% of yttria using high-energy ball milling in planetary mill under an air and Ar atmosphere. During mechanical alloying of composite powder in air atmosphere cracking of powder particles predominated over alloying and very fine composite powder was prepared having limited formability in green state. Dense samples of 17Cr-1Mo ODS steel having uniform distribution of yttria particles of size up to 10 nm were prepared from composite powder alloyed under Ar atmosphere for 12 hours and 24 hours. The ferritic microstructure with particle size about 1 μm was prepared from powder milled for 12 hours. Distinctive plastic deformation after 24 hours of milling led to finer ferritic grain structure development having particle size about 500 nm.*

**Keywords:** ODS steel, mechanical alloying, hot rolling

### INTRODUCTION

The iron-base superalloys, based on oxide dispersion strengthened (ODS) steels, were introduced in the end of '70<sup>s</sup> by INCO company for high-temperature applications [1,2]. These steels having nominal chemical composition 14-20Cr-Mo(Al)-Ti-Y<sub>2</sub>O<sub>3</sub> were developed as direct successor of 9Cr-1Mo HT91 steel and combine high-temperature strength and stability of oxide dispersion with excellent resistance to surface oxidation. These steels based either on ferritic-martensitic 9Cr or ferritic 14Cr ODS steels are nowadays under consideration as a tubing material for IV generation of fission reactors and as a structural material for developed fusion reactors. ODS steels contain small amounts (about 0.25 wt.%) of homogeneously dispersed nano-size yttria particles, to increase the creep strength of the steel [3]. Moreover, the yttrium-rich nanoparticles effectively suppress softening annealing by blocking dislocations motion at elevated temperatures [4,5]. The ODS steels are prepared from blend of atomic powders and master alloys powders in ratio of the steel by mechanical alloying process. During alloying process the composite powder consists of homogenous solid solution of starting materials is obtained subsequently high-temperature compacted to dense steel. The yttrium oxide dispersion it is possible to create either by internal oxidation from yttrium atoms distributed in the composite powder during high-temperature compaction or by des-integration of yttria particles directly added to the

blend of starting powders [6,7]. The aim of this work was to verify preparation of ferritic Cr-Mo ODS steel by mechanical alloying from commercially available pre-alloyed AISI 434 steel powder. The two ways of oxide dispersion development in the steel were proven – by internal oxidation of yttrium and by yttria adding. The results obtained confirmed that ferritic ODS steel can be prepared from pre-alloyed steel powder by introducing of yttria particles by means of mechanical alloying process.

## EXPERIMENTAL

The 17Cr-1Mo ODS steel was prepared by mechanical alloying from commercially available AISI 434 steel powder (434LHC, Höganäs) having chemical composition 16.8Cr-1Mo-0.8Si. The ODS composite powder was prepared by adding 0.25 wt.% of metallic yttrium powder (Sigma-Aldrich) (composite powder denoted as „434Y“) or by adding 0.25 wt.% of yttria (Verochem) (composite powder denoted as „434Y<sub>2</sub>O<sub>3</sub>“). The blend of powders was mechanically alloyed up to 24 h using planetary ball mill Pulverisette P-6 (Fritsch) in hardened steel vial with steel balls. To ensure the oxide input, the mechanical alloying of 434Y composite powder was conducted in air atmosphere. During mechanical alloying of the 434Y<sub>2</sub>O<sub>3</sub> composite powder the milling vial was filled with Ar at 2 atm. The ball-to-powder ratio was 15:1 and rotational speed of main disc was 350 rpm. The microstructure of the composite powders was observed by means of scanning electron microscopy (SEM, JEOL 6460 with Oxford Instruments INCA Energy EDX). Particle size of composite powders prepared was evaluated by means of SEM images analysis using ImageJ software. Vickers hardness of the powders and bulk samples was studied by means of instrumented hardness tester (ZHU Zwick/Roell) under load 0.1 kg according to the EN ISO 6507 standard. The two kind of dense bulk samples were prepared. For compaction measurements the cylindrical shape samples with dimensions of  $\varnothing 10 \times 3$  mm (d  $\times$  h) were prepared by cold compaction by uni-axial compaction under load of 50-800 MPa. The bulk dense samples of ODS steel were prepared by hot-rolling at 1200°C of composite powders encapsulated in mild steel containers. Apparent densities of powders were measured using weighing of certain amount of powder poured into graduated cylinder. The green densities of these samples were evaluated by dimensions measurement method. The final bulk samples were prepared by hot rolling. The composite powder was canned in mild steel container and rolled at 1200°C. No additional heat treatment was applied to the samples.

## RESULTS AND DISCUSSION

The 434LHC steel powder using for mechanical alloying consists of particles having size in range 10  $\mu$ m – 300  $\mu$ m and mean size about 50  $\mu$ m (Fig.1 and Fig.2).

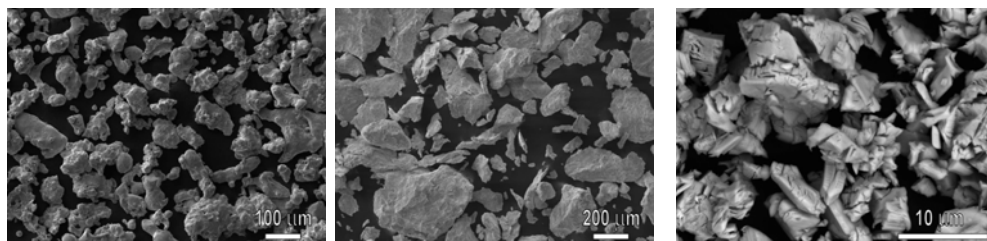


Fig.1. Starting powders used for composite powders preparation (434LHC steel – left; metallic yttrium – middle; yttria - right).

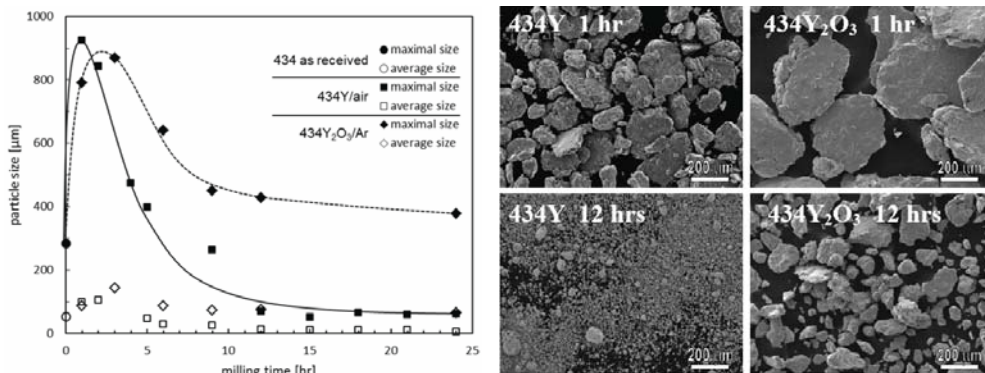


Fig.2. Dependence of particle size of composite powders 434Y and 434Y<sub>2</sub>O<sub>3</sub> on milling time (left) and evolution of corresponding particle shape (right) during milling.

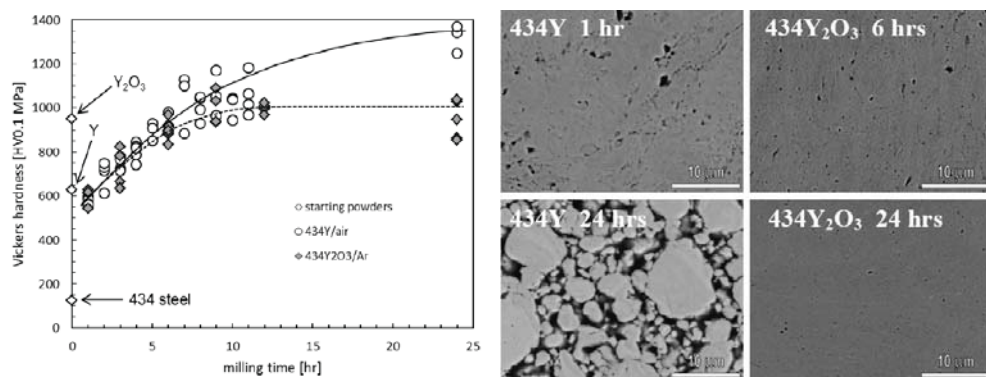


Fig.3. Dependence of hardness of composite powders 434Y and 434Y<sub>2</sub>O<sub>3</sub> on milling time (left) and change microstructure of composite powders during milling (right).

Starting hardness of 434 steel powder was about 125 HV0.1 (Fig.3). During first 3 hrs of mechanical alloying both under air and Ar atmosphere the powder particles were cold welded together under impact and shear forces between milling balls forming large particles of size around 800 μm (see Fig.2). As mechanical alloying continued the particles got harder due to severe plastic deformation (see Fig.3). Due to plasticity consumption the powder particles were then fractured rather than welded together. This behaviour occurred between 3 hrs and 9 hrs of milling in the case of 434Y<sub>2</sub>O<sub>3</sub> powder milled under Ar atmosphere. After this period of milling the balance between welding and fracturing was achieved and size and hardness of 434Y<sub>2</sub>O<sub>3</sub> composite particles remains constant (compare Fig.2 and Fig.3). The 434LHC powder milled in air atmosphere exhibited faster decrease of particle size after culmination of particle size due to oxidation of surfaces revealed during fracturing of particles. The oxidized surfaces prevented cold welding and thus 434Y composite powder was finer than starting 434LHC powder (see Fig.2). As a result of powder oxidation the hardness of 434Y composite powder did not reach the steady value and rather than alloying the milling process prevailed and very fine composite powder with gradually increasing hardness was produced by mechanical alloying process (see microstructure in Fig.3). It is assumed that during repeating welding-fracturing process the starting powders are thoroughly blended. Alloying phase (Y or Y<sub>2</sub>O<sub>3</sub>) can be effectively

distributed through the matrix just if the hardness of matrix is equal or slightly higher to the hardness of alloying phase to achieve mutual plastic deformation and fracturing of matrix and alloying phase. During mechanical alloying, the hardness of 434LHC powder increased due to plasticity consumption of the powder. During milling of 434LHC powder in air atmosphere, the level of hardness of metallic yttrium was achieved in the first hour of milling. On the other side the hardness of matrix 434LHC powder achieved the level of hardness of yttria after six hours of milling, the joinability of matrix powder was preserved due to protective environment of Ar (see microstructure in Fig.3). Apparent densities of both starting 434LHC powder and powders after milling were comparable and were about 48% of theoretical density (t.h.).

Dependence of green density of uni-axially compacted bulks on pressure are given in Fig.4. The green density of starting powder (hardness about 125 HV0.1) gradually increased with pressure used for uni-axial pressing from 52% t.h. at 50 MPa to 88% t.h. at 800 MPa. The green densities of 434Y composite powder varied with pressure just slightly from 60%t.h. at 50 MPa to 65%t.h. at 500 MPa and it was comparable with green densities variation of pure 434LHC powder milled in air atmosphere at the same conditions. This behaviour was caused both by high hardness of 434Y composite powder (coming from severe plastic deformation) and by fine particle size (caused by oxidation during mechanical alloying). The 434Y powder thus had very limited formability in green state. The dependence of green density of 434Y<sub>2</sub>O<sub>3</sub> composite powder varied with pressure from 60% t.h. at 100 MPa to 77% t.h. at 1100 MPa and lied between dependence of as-received powder and powder milled in air atmosphere. The limited formability of composite powders was caused by their high hardness (1000HV0.1 and 1300HV0.1 for 434Y<sub>2</sub>O<sub>3</sub> and 434Y respectively) compared to starting 434LHC steel powder (185HV0.1). Annealing of the starting 434LHC and composite 434Y powders was conducted under protecting H<sub>2</sub> atmosphere at 300°C, 500°C and 800°C for 1 hour. As is evident from dependence of Vickers hardness of powders on temperature no annealing of dislocation structure resulting in hardness decreasing occurred. The dislocations were probably pinned by stable dispersion of yttria nano-particles presented in microstructure of composite powder. For bulk samples preparation 434Y<sub>2</sub>O<sub>3</sub> composite powder was used. The powder was placed to the tubular container made of mild steel having inner diameter of 8 mm and wall thickness of 1 mm. The container was tightly welded and hot rolled at 1200°C through die having cross-section 14×2 mm<sup>2</sup>. The cross-section reduction of 65% led to extensive 3D deformation of powder particles and compaction of powder to dense ODS steel. The microstructure of densified 434Y<sub>2</sub>O<sub>3</sub> composite powder mechanically alloyed for 12 hours and for 24 hour is given in Fig.5. The ODS steel from powder milled for 12 hours consisted of grains having size about 1 µm. On the other hand the ODS steel from powder milled for 24 hours had considerably finer grain structure consisted of grains having size about 500 nm. During steady phase of mechanical alloying between 12 hours and 24 hours of milling, the microstructure of powder particles is steadily refined by introducing of dislocation through plastic deformation of particles. The accumulation of dislocation introduces low angle grain boundaries into material. During hot compaction the yttria particles then serves as obstacles both for dislocation and grain boundaries motion. The TEM pictures of compacted 434Y<sub>2</sub>O<sub>3</sub> powder given in Fig.6 showed uniform distribution of yttria particles having size up to 10 nm in ODS steel microstructure. In detailed picture, the dislocations pinned in yttria nano-particles are clearly visible.

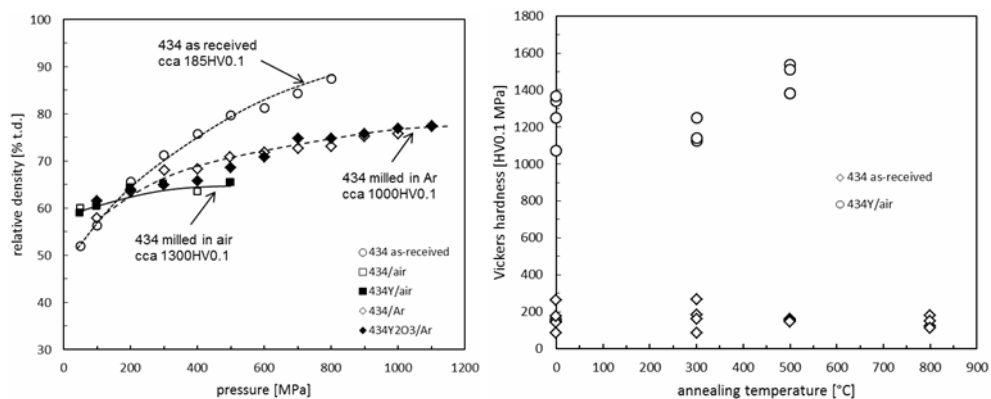


Fig.4. Dependence of green density of starting 434LHC steel powder and composite powders prepared on pressure of uni-axial compaction (left) and dependence of hardness of starting 434 powder and composite powder 434Y on annealing temperature (right).

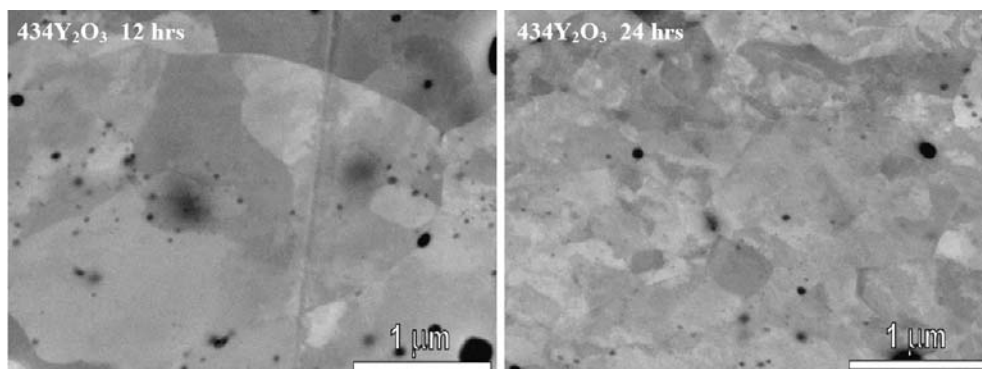


Fig.5. Microstructure of bulk 434Y<sub>2</sub>O<sub>3</sub> ODS steel after hot-rolling compaction (12 hrs milled powder – left; 24 hrs milled powder - right).

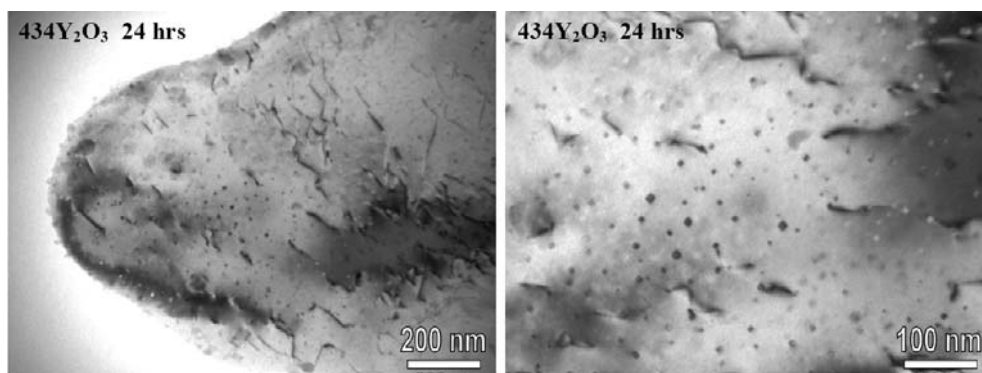


Fig.6. Oxide dispersion in bulk 434Y<sub>2</sub>O<sub>3</sub> ODS steel after hot-rolling compaction (24 hrs milled powder).



## CONCLUSIONS

The 17Cr-1Mo-Y<sub>2</sub>O<sub>3</sub> composite powder was prepared from commercially available AISI 434LHC steel powder by adding 0.25 wt.% of metallic yttrium or by adding 0.25 wt.% of yttria. The composite powders were produced by mechanical alloying using high-energy ball milling in planetary mill under an air and Ar atmosphere and subsequently consolidated by hot rolling. During mechanical alloying of composite powder in air atmosphere cracking of powder particles predominated over alloying due to oxidation of surfaces revealed during their fracturing. As a consequence of this, the very fine composite powder was prepared having limited formability in green state. Dense samples of 17Cr-1Mo ODS steel having uniform distribution of yttria particles of size up to 10 nm were prepared from composite powder alloyed under Ar atmosphere for 12 hours and 24 hours. The ferritic microstructure with particle size about 1 µm was prepared from powder milled for 12 hours. Distinctive plastic deformation after 24 hours of milling led to finer ferritic grain structure development having particle size about 500 nm.

## Acknowledgement

This work was realized in CEITEC - Central European Institute of Technology with research infrastructure supported by the project CZ.1.05/1.1.00/02.0068 financed from European Regional Development Fund, financially supported by the Czech Science Foundation project No. 14-25246S and Slovak Research and Development Agency under the contract no APVV 0222/10 and project VEGA 2/0155/12.

## REFERENCES

- [1] Benjamin, JS.: US Patent 3,591,362 (1971)
- [2] Fischer, JJ.: U.S. Patent 4,075,010 (1978)
- [3] Hayashi, T. et al.: Acta Materialia, vol. 56, 2008, p. 1407
- [4] Hoelzer, DT. et al.: Journal of Nuclear Materials, vol. 367-370, 2007, p. 166
- [5] Klueh, RL. et al.: Journal of Nuclear Materials, vol. 307-311, 2002, p. 773
- [6] El-Genk, MS., Tournier, JM.: Journal of Nuclear Materials, vol. 340, 2005, p. 93
- [7] Oksiuta, Z., Baluc, N.: Journal of Nuclear Materials, vol. 374, 2008, p. 178