INVESTIGATION ON MECHANICAL ALLOYING PROCESS FOR V-CR-TI ALLOYS

MADALINA STANCIULESCU1, PAULA CARLAN1, MARIOARA ABRUDEANU2, A. GALATEANU3, MARIA MIHALACHE1, G. BUCSA1

[1]Institute for Nuclear Research,Câmpului Street, No.1, Mioveni, Arges, Romania
[2]University of Pitesti, Targu din Vale Street, No.1, Pitesti, Arges, Romania
[3]National Institute of Materials Physics, Atomistilor 105 bis, Magurele, Romania

mada.stanciulescu@nuclear.ro

ABSTRACT

Mechanical alloying (MA) is an efficient approach for fabricating oxide-dispersion alloys and structural materials including vanadium alloys for fusion and fission application. Dissolution behaviour of the alloying elements is a key issue for optimizing the mechanical alloying process in fabricating vanadium alloys. This paper studies the MA process of V-4wt.%Cr-4wt.%Ti alloy. The outcomes of the MA powders in a planetary ball mill are reported in terms of powder particle size and morphology evolution and elemental composition. The impact of spark-plasma sintering process on the mechanically alloyed powder is analysed. An optimal set of sintering parameters, including the maximum temperature, the dwell time and the heating rate are determined.

Key words: vanadium alloys, mechanical alloying, spark plasma sintering

Introduction

Vanadium alloys are attractive structural materials for fusion reactors due to their outstanding properties, especially the low induced activation and high temperature strength.

Power plant components are commonly fabricated by conventional metallurgical processing methods including: casting, rolling, forging, extrusion or welding. Although these processing methods have been improved over the years enabling them to produce high quality products, their limitations resulting from grain growth, internal shrinkage, rolling texture or residual stresses have never been fully resolved [1].

Grain size refining and nanoparticle dispersion by using mechanical alloying can efficiently strengthen vanadium alloys. Recently, researchers examined V, V-Cr, V-Ti and V-W systems with Y additions. Studies on the mechanical alloying (MA) process of a V matrix with 4%wt.Cr and 4%wt.Ti addition were carried out. It is believed that V-4Cr-4Ti alloy is more suitable than the above alloy systems because Ti can promote low swelling and Cr enhances oxidation resistance and solid solution hardening [2].

The purpose of this paper is to test the possibilities of obtaining V-Cr-Ti alloy by mechanical alloying using a high energy ball mill. The studied material is a V-4wt.%Cr-4wt.%Ti alloy. The vanadium-based alloy is manufactured by the following major steps: (I) the mechanical alloying (MA) of the elemental powders, (II) the consolidation of the powder by spark plasma sintering (SPS). This consolidation technology has several specific features that distinguish it among other methods: the particular influence of the electric current on the material properties, the high speed of the process that achieves the minimum

grain growth, the ability to control any stage of sintering, and the uniformity of properties throughout the sample volume [3].

Experimental

The powders used in this study include vanadium (99.5%, -325mesh), chromium (99.2%, APS<10micron) and titanium (99.99%, -325mesh) supplied by Alfa Aesar. The powders are mixt to yield compositions of V-4%wt.Cr-4%wt.Ti in argon atmosphere. A planetary mill is used as mechanical alloying equipment with a set of stainless steel mill vessels and balls. The ball-to-material weight ratio used is 10:1. The powders are milled for 72 hours milling time, at a rotation speed of 400rpm in cycles of 10min milling and 5min pause and argon protective atmosphere. It is used 1ml of anhydric alcohol to soak 5g of powder. After ball milling the powder is compacted by spark-plasma sintering (SPS). For the consolidation and sintering, 12 DC train pulses of 3msec and 3msec pause are used. The maximum current is 1.9 kA at 4.4V. The sintering process is realized in vacuum after a spallation with argon. The powder is protected against contamination by graphite (from the die) by covering the major surfaces of the die with 0.025mm tantalum foil. The sintered samples are mechanically polished.

After MA, microstructural evolution of particles and element distribution are analyzed by Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray Spectroscopy (EDX) analyses. Changes in the material composition are analyzed by X-ray diffraction (XRD). Crystallite size distribution and lattice microstrain are analyzed by Warren-Averbach method. The effect of the SPS process is analyzed and the relative density of the samples is measured.

Results and discussions

- **Effect of mechanical alloying**

Figure 1 shows a typical XRD spectra of V-4 wt.% Cr-4 wt.% Ti before and after the mechanical alloying process. In this plot, after 72h milling, the peaks of the alloying elements have mostly disappeared, but a small part of the titanium powder remains unalloyed. Also, the diffraction analysis shows a contamination of the alloyed powder with Fe from the stainless steel vessel and milling balls.

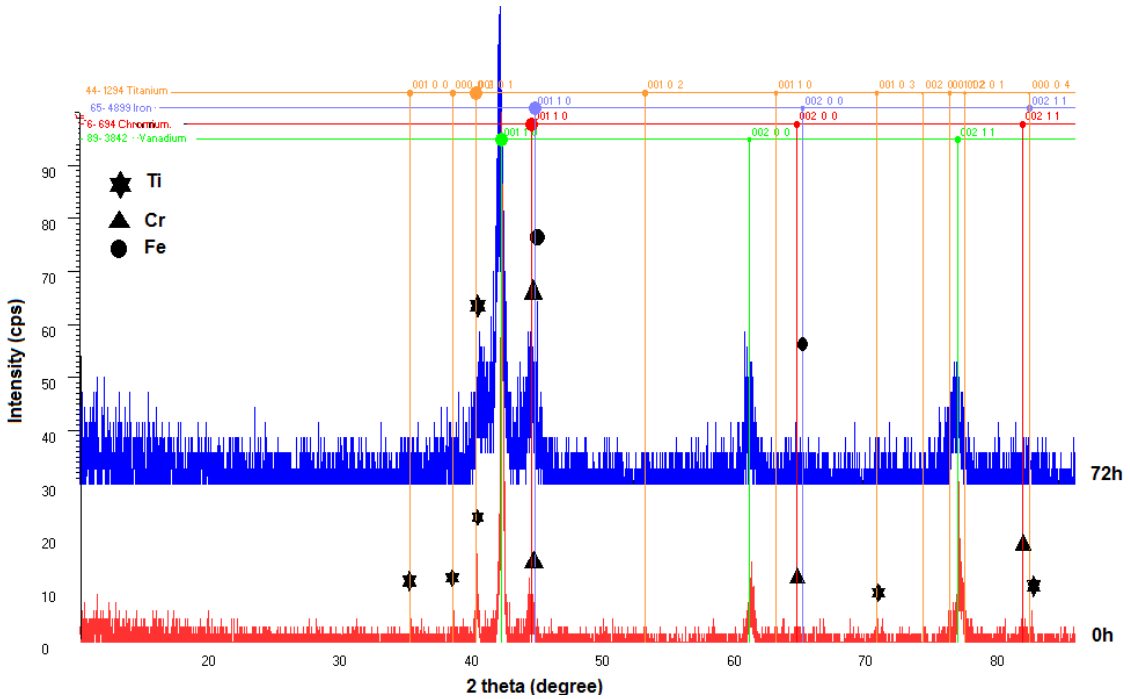

Figure 1 *XRD spectra for V-4%wt.Cr-4%Ti before and after 72h milling*

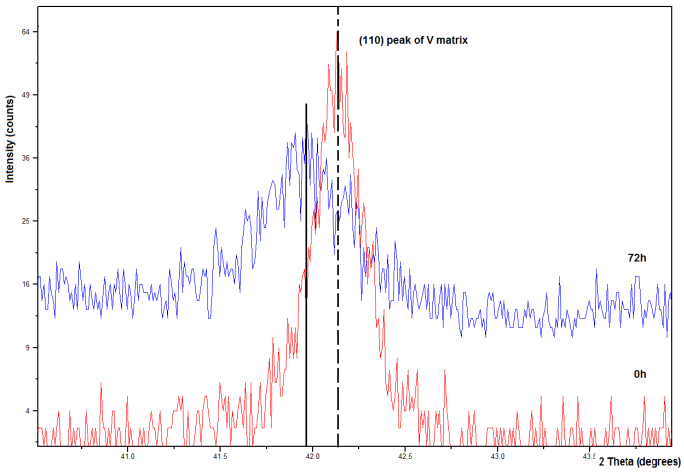

Fig.2. *Typical XRD peak shift of V matrix during MA process*

Figure 2 shows typical (110) peak shifts of the V matrix during the MA process with stainless steel balls. The peak shifts to a lower angle after milling, meaning that the lattice parameter value increases expanding the V lattice.

Atoms those are large relative to vanadium (atomic radius: 0.132nm), such as Ti (atomic radius: 0.143nm) expands the V lattice, while smaller atoms such as Cr (atomic radius: 0.125nm) causes lattice shrinkage. The expansion of the lattice determines the growth of the lattice parameter and of the interplanare space which involves the displacement of the peak positions to lower angles. For the shrinkage of the lattice the displacements is to higher angles. As (110) peak shifts to lower angle after milling, Ti is the last element to change the lattice parameter determining the expansion of the V matrix lattice. A possible dissolution history of Cr and Ti in the V matrix is that Cr dissolves first and then Ti.

This is in concordance with the studies realised by P.F. Zheng [2] which determined that the collision-induced dissolution rate of Cr is higher than that of Ti. This dissolution of the elements also agrees with composition analyses determined by XRD.

The crystallite size distribution and lattice microstrain are determined by Warren-Averbach analyses with X'Powder program using the diffraction data. The crystallite size can be calculated by Scherrer equation as a function of the diffraction peak width (specified as the full width at half maximum peak intensity -FWHM), peak position and wavelength of the used radiation. Warren-Averbach method takes not only the peak width into account but also the shape of the peak. This method is based on a Fourier deconvolution of the measured peak and the instrument broadening to obtain the true diffraction profile. This method is capable of yielding both the crystallite size distribution and lattice microstrains. The Warren-Averbach method is based on a Fourier analysis of the diffraction peak. The measured peak profile is actually the convolution of a function for the pure peak profile and the function for the instrumental broadening. A plot of the cosine coefficients and the length of a column of unit cells perpendicular to the diffracting planes is used to determine the area weighted crystallite size and lattice microstrain. If two peaks in the same family of planes are used in this analysis then the contribution of microstrain to peak broadening can be eliminated. By these analyses is determined that the raw materials crystallite size is 57.9 nm for V, 58.1nm for Cr and 51.3nm for Ti and the mean square strains related to the Fourier Length (L) are 0.4%, 0.3% and 0.4%, respectively.

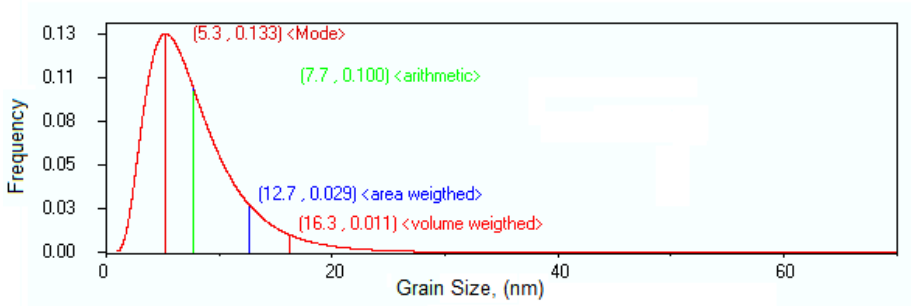

Figure 3. *Log normal distribution of the crystallite size after milling*

The size distribution and the characteristic averages after the milling process are shown in **Figure 3**. After the MA process the crystallite size decreases to 12.7 nm. The mean square strain related to the Fourier Length increases to 0.6% compared with the ones of the initial lattice microstrain. The milling process takes place with the destruction of the crystal lattice, since the crystallite size decreases.

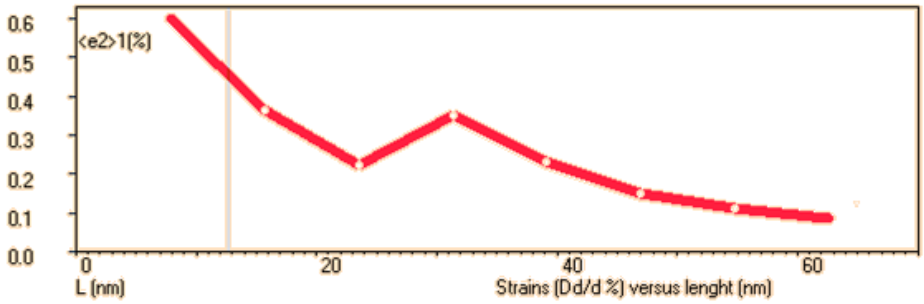

Figure 4 *The evolution of lattice microstrain after milling*

The microstructural evolution of the initial powders after 72h milling is analyzed by Scanning Electron Microscopy. **Figures 4a,b,c** shows the initial V, Cr and Ti powders microstructure and particle size revealing that V (**Figure 4a**) and Cr (**Figure 4b**) are very agglomerated, fine powders with an average particle size <1μm, but Ti particles exceed 100 μm.

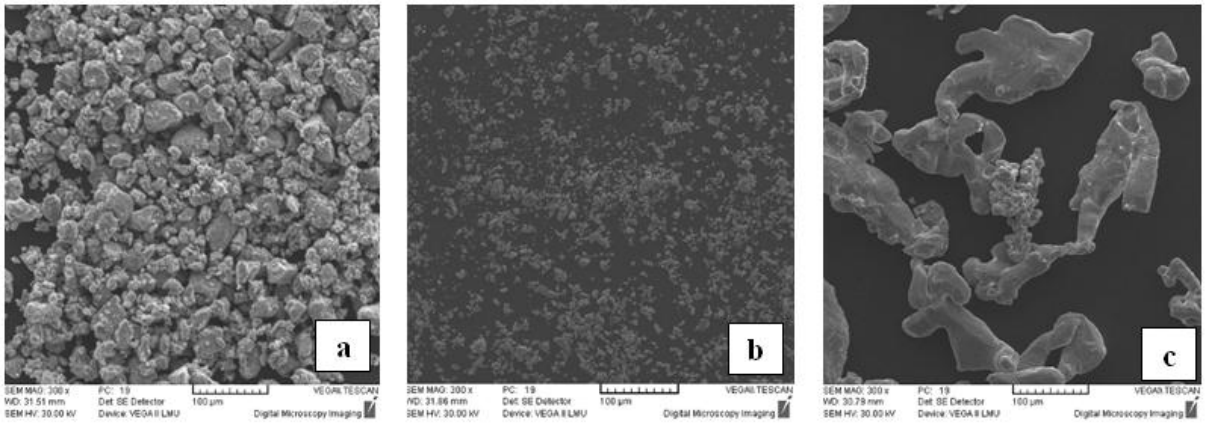

Figure 4 *SEM images of the a)V, b) Cr and c)Ti powders before the mechanical alloying process*

In the **Figures 5a,b** it is seen that after milling the grain size is variable ranging from some micron to hundreds of microns for the biggest particles. This reveals that the very fine initial powders weld together to form particles which have an average size of 200-250μm. This is in concordance with the theory that in the initial milling stages ductile particles get flattened and weld together by ball-powder-ball collisions and this leads to an increase in particle size, and with continued milling the particles are refined and the grain size decreases [4, 5]. Continued milling it is necessary to refine the particles that reach 400-500μm. The detailed micrograph (**Figure 5c**) of the milled powder shows that a plastic deformation of the particle takes place.

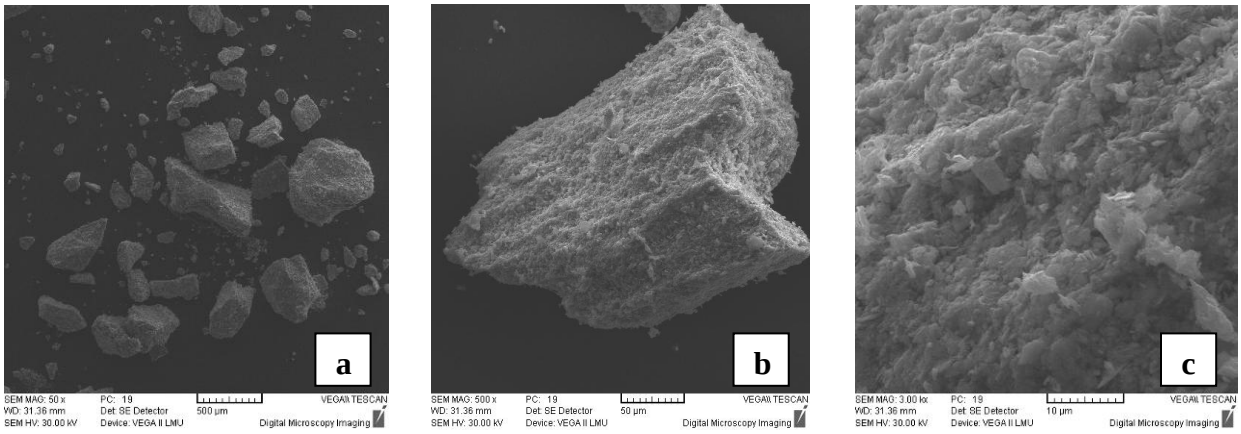

Figure 5 *SEM images of the mechanically alloyed powder at different magnitudes*

Figure 6 shows the element distribution of the mechanically alloyed powder analyzed by (EDX). V and Cr are distributed rather uniformly, but Ti looks less homogeneous, showing that Cr dissolves faster than Ti in the V matrix. Thought the higher-Ti-concentration areas, homogeneous dissolution of Ti is expected with a longer MA time. The EDX analyses reveal the presence and non-uniformity of the Fe that contaminated the milled powder. The EDX results are in concordance with ones obtained by XRD analyses.

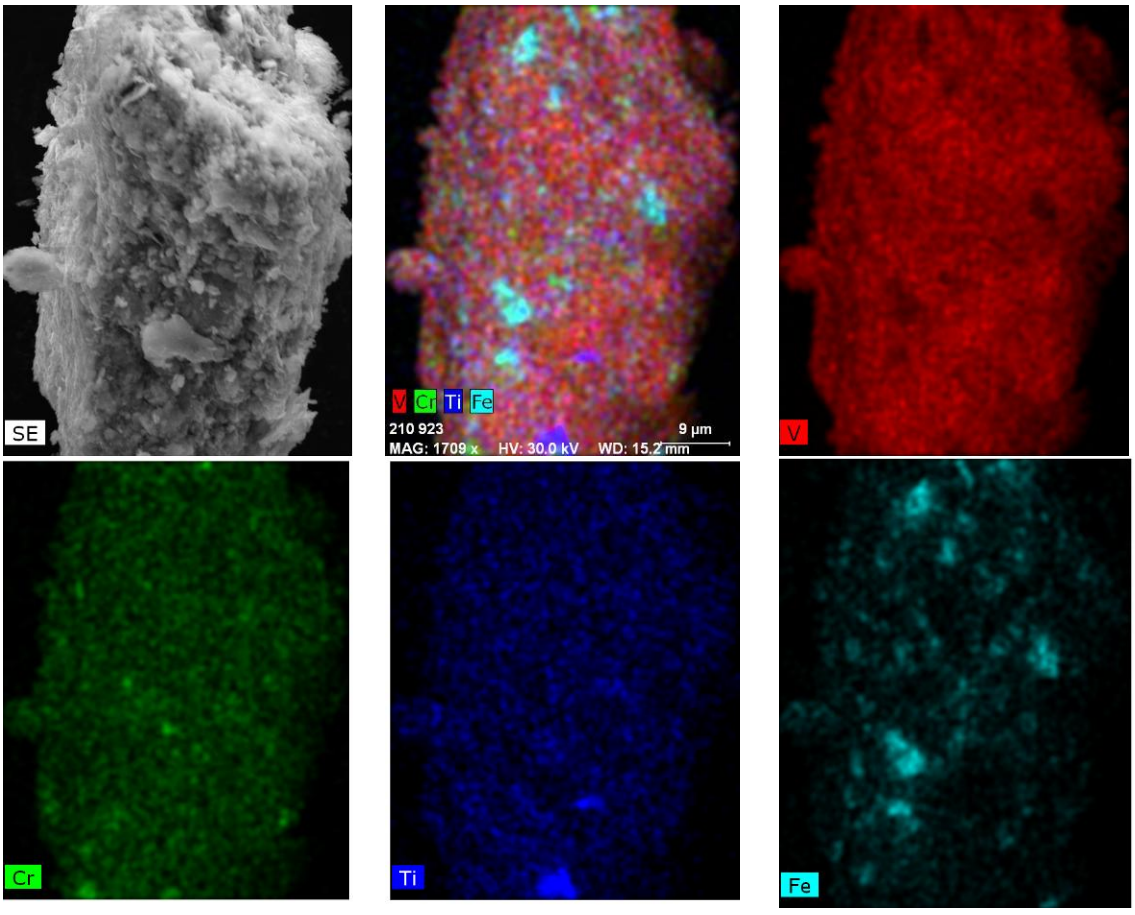

Figure 6 *Elements distribution map for 72 h V-4%Cr-4%Ti milled powder*

Thus, it is clear that the time of mechanical alloying affects the final powder particle size and the distribution elements in the final composition. This study indicates that the alloying parameters determine the final characteristics of the MA material and those should be chosen appropriately to obtain a homogeneous material and to avoid the contamination.

Effect of the sintering process

The MA powder was sintered by SPS at different temperatures and pressures to find out the proper process parameters. The final temperature and pressure sintering regime is shown in **Figure 7**. A heating rate of 100ºC/min and a holding time of 5 min were used for the experiment. The maximum temperature used is of 1200°C and the force of 12kN.

A good compaction is obtained in the sintering process. The theoretical density (TD) of the solid V-4%Cr-4%Ti was assumed to be 6.088g/cm^3 and the density obtained for the sintered sample reached over 99.3% TD at 1200ºC and 12kN.

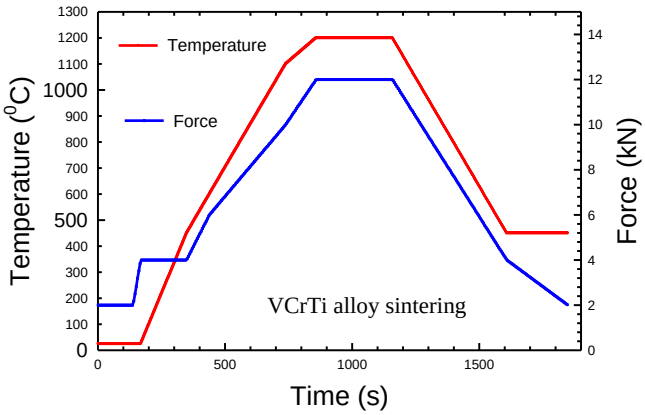

Figure 7 *Sintering process of the milled powder*

After spark plasma sintering the maximum peak of the mechanically alloyed powder shifts to a higher angle compared to the MA powder maximum peak (**Figure 8**). It is possible that the Fe atoms (atomic radius: 0,126nm) entered in the V lattice causing the shrinkage of the lattice. The XRD analyses show that at high temperatures, during the sintering process, V combines with C atoms (from the die) to form vanadium carbides and that because V has a very high affinity for carbon. It is necessary to avoid carbon contamination in SPS process.

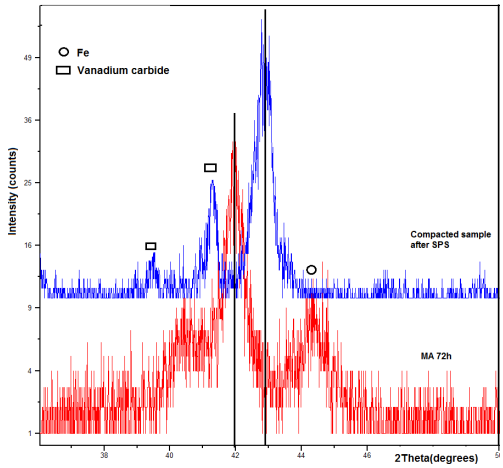

Figure 8 *Typical XRD maximum peak shift of MA powder after SPS process*

Conclusions

The mechanical alloying and spark plasma sintering processes of V-4Cr-4Ti powder were studied. The dissolution behaviour of the alloying elements in the V matrix and de effect of milling process and milling tools are discussed.

Based on this study, the conclusions of this paper are the following:

- It was found that during the MA process particles weld together and this leads to an increase in the particle size up to 500µm for the biggest particles and an average size of 200-250µm. With continued milling, the particles can be refined to nanometer size.
- In the MA process a change of crystal lattice takes place by increasing the network defects and deformation. After milling, there was a decrease in the crystallite size to 12.7nm, compared with the one of the original crystallites. The lattice microstrain induced by ball-powder-ball collision increases during MA processing from 0.4% (before milling) to 0.6% (after milling).
- The collision-induced dissolution rate of Cr into the V matrix is higher than that of Ti. The poor dissolution of Ti particles retards the V-4Cr-4Ti solid solution formation. Higher collision intensity and longer MA time might be necessary to dissolve the Ti particles completely, but this can determine a higher contamination of the alloy during MA.

- Stainless steel balls can be incorporated in the V matrix and contaminate the alloy during MA process. The contamination can be avoided by adjusting the milling process parameters as rotation speed, milling time etc.
- The sintering process involved a possible dissolution of Fe into the V matrix and the contamination of the samples with carbon from the sintering die.

References

[1] Corwin, W.R., et al., Generation IV Reactors Integrated Materials Technology Program Plan: Focus on Very High Temperature Reactor Materials, ORNL/TM- 2008/129- Oak Ridge National Laboratory;

[2] P.F. Zheng, T. Nagasaka, T. Muroga, J.M. Chen, Investigation on mechanical alloying process for vanadium alloys, journal of nuclear Materials 442, 2013, p.S330-S335

[3] I. Bogachev, E. Grigoryev, O.L. Khasanov, E. Olevsky, Fabrication of 13Cr-2Mo feritic/martensitic oxide-dispersion-strengthened steel components by mechanical alloying and spark plasma sintering, JOM, Vol.66, 2014, p.1020-1026

[4] C. Suryanarayana, Mechanical alloying and milling, Progress in Materials Science 46, 2001, p. 1-184

[5] M. Sherif El-Eskandarany, Mechanical alloying for fabrication of advanced engineering material, Published in the United States of America by Noyes Publications / William Andrew Publishing, 2001, p.5-19