Dissolution Behaviour of Alloying Elements Into Vanadium Matrix During Mechanical Milling

MADALINA STANCIULESCU1,2*, MARIAROA ABRUDEANU2, ANDREI GALATANU1, PAULA CARLAN1, MARIA MIHALACHE1

1Institute for Nuclear Research, 1 Campului Str., 115400, Pitesti, Romania
2University of Pitesti, 1 Targu din Vale Str., Pitesti, Arges, Romania
3National Institute of Materials Physics, Atomistilor 105 bis, Magurele, Romania

Mechanical alloying (MA) is an efficient approach for fabricating ODS alloys and structural materials including vanadium alloys for fusion and fission applications. Dissolution behavior 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, morphology and composition evolution. The impact of spark-plasma sintering process on the mechanically alloyed powder is analyzed. The microstructure of the V-4wt.%Cr-4wt.%Ti alloy prepared by mechanical milling is investigated with a X-ray diffractometer and scanning electron microscope.

Keywords: vanadium alloys, mechanical alloying, spark plasma sintering

Vanadium alloys and in particular the V-Cr-Ti alloys have been extensively studied for applications in fusion reactors because of good mechanical properties, low activation and good stability under irradiation above 673K [1-3]. Vanadium alloys are also attractive structural materials in advanced fission reactors such as Sodium Fast Reactors, SFRs, and Gas Fast Reactors, GFRs, with the nominal temperature between 673 K and 1073 K for fuel cladding and ducts consistent with the operating window of V-4Cr-4Ti alloys (673-1023K [4]) [1,5]. Considerable steps forward has been made towards development of vanadium alloys. Much of the recent research has focused on vanadium alloys containing 4–5%Cr and 4–5%Ti, but a number of alternative compositions and processing routes have been explored in an effort to achieve improved performance for fusion.

The major remaining issues for vanadium alloys are mainly thermal and irradiation creep, helium effects on high temperature mechanical properties and radiation effects on low temperature fracture properties. In fact, they are a good concession between refractory features up to 973K, compatibility with a fast spectrum, and accessible machining/shaping processes. Achievement of vanadium alloys in GFRs and SFRs is currently under deliberation and must be estimated, particularly concerning the new requirements of these applications (atmosphere, temperature, loading, etc.).

Progress on microstructural control by advanced powder metallurgy methods makes possible the fabrication of ultrafine grained and particle dispersed V-base alloys [6]. Recently, researchers examined V, V-Cr, V-Ti and V-W systems. Studies on the mechanical alloying (MA) process of a V matrix with 4%wtCr 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. Grain size refining and nanoparticle dispersion by using mechanical alloying can efficiently strengthen vanadium alloys [7,8]. It was shown that resistance to radiation embrittlement in refractory metals can be improved by introducing fine grain microstructures and dispersed particles. In addition, fine grains can contribute to improve high temperature strength [9].

The purpose of this paper is to study the dissolution behaviour of Cr and Ti into the vanadium matrix during the mechanical alloying process and to investigate the possibilities of obtaining fine-structure V-Cr-Ti alloy by this method. The studied material is a V-4wt.%Cr-4wt.%Ti alloy. The vanadium-based alloy is prepared by mechanical alloying in a planetary ball mill starting from the V, Cr and Ti elemental powders and the consolidation of MA 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 [10].

Experimental part

The powders used in this study include vanadium (99.5% purity, < 44µm), chromium (99.2% purity, < 10µm) and titanium (99.99% purity, < 44µm) supplied by Alfa Aesar. The powders are mixt to yield compositions of V-4wt.%Cr-4wt.%Ti. 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 48 hours milling time, at a rotation speed of 400 rpm, in an Ar argon atmosphere and 1mL of anhydric alcohol is used to soak 5g of powder.

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). The crystallite size distribution and lattice microstrain are determined from the diffraction line profile analyses.

X-ray diffraction line profile analysis is an adapted tool to characterize the behaviour of powders under mechanical alloying process. The most used method to extract the size of the coherent diffracting domain from diffraction peak is Scherrer equation (1) [11]:

\[
L = \frac{K \lambda}{FWHM \cos \theta}
\]
where $K$ is a constant close to unit, FWHM is specified as the full width at half maximum of the peak, $\theta$ the peak position and $\lambda$ the wavelength of the used radiation.

But in almost all cases line broadening occurs due to size and lattice distortion effects. One way to separate these effects has been developed by Warren-Averbach method which is an approach of size and strain analysis using the deconvolution of the structural line profile and the Fourier transform for evaluation of the coherent domain and strain. The real Fourier coefficient is the product of one term dependent on the length of columns of unit cells $L$ and another term related to the deformation in the crystal lattice which depends on $1/d$ ($d$ - interplanar distance), dependent therefore on the order of the reflection of the profile considered. The real Fourier coefficient is [12]:

$$A(L, \frac{1}{d}) = A^s(L) \cdot A^p(L, \frac{1}{d})$$  \hspace{10mm} (2)

Equation (2) can be written as:

$$\ln A(L, \frac{1}{d}) = \ln A^s(L) - 2\sigma^2 \cdot \left(\frac{1}{L}\right)^2$$  \hspace{10mm} (3)

where $\sigma^2$ is the mean square strain related to $L$. Using at least two reflections it is possible to separate the two coefficients on a graph of $\ln A(L, \frac{1}{d})$ versus $\left(\frac{1}{L}\right)^2$ [12].

The X'Powder program allows determination of the crystallite size and crystal lattice deformation by Warren-Averbach method. This program is used to analyze the elemental and mechanically alloyed powders.

After ball milling the powder is compacted by spark-plasma sintering (SPS). For the consolidation and sintering, 12 DC train pulses of 3ms and the maximum current is 1.9 kA at 4.4V. 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. The effect of the SPS process is analyzed and the relative density of the samples is measured.

Results and discussions

Evolution of microstructure and composition during milling

The typical XRD patterns obtained for V-4 wt.% Cr-4 wt.% Ti before and after the mechanical alloying process are compared in figure 1. The Ti and Cr peaks are clearly observed in the initial mixt powder, whereas they have mostly disappeared in the MA processed material, but a small part of the titanium remains unalloyed. In addition, the diffraction analysis evidences a contamination of the milled powder with Fe from the stainless steel vessel and milling balls.

During the MA process a shift of the typical (110) peak of the V matrix is observed (fig. 2). The peak shift toward a lower angle reveals that lattice parameter value increases expanding the V lattice. It is known that the atoms which 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 interplanar 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 Zheng [7,8] which show that collision-induced dissolution rate of Cr is higher than that of Ti when mechanically alloying V, Cr, Ti and Y elemental powders in a planetary ball mill.

The X-ray diffraction line profile analysis of the elemental powders with the X'Powder program (Warren - Averbach module) shows that the crystallite size of V, Cr and Ti are 57.9 nm, 58.1nm and 51.3nm, respectively and maximum strain related to the Fourier length ($L$) are 0.4, 0.3 and 0.4%, respectively.

The log-normal distribution and the crystallite size weighted by area (area weighted mean crystallite size) for the milled powder are given in figure 3. After the MA process the crystallite size decreases to 12.7 nm and the maximum strain ($\epsilon^2$) related to the Fourier length ($L$) is 0.4%.
length (fig. 4) increases to 0.6% compared with the one of the initial powders. Therefore, the milling process involves the destruction of the crystal lattice, since the crystallite size decreases.

Morphology of the elemental powder particles is presented in figure 5. The microstructural evolution of the powder particles is analyzed after 48h milling. According to figure 6a,b, after milling the grain size is variable ranging from some micron to hundreds of microns for the biggest particles. Accordingly, the elemental powders weld together, which 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. With continued milling the particles can be refined and the grain size decreases [13,14]. Continued milling it is necessary to refine the particles that reach 400-500µm. The detailed micrograph (fig.6c) of the milled powder shows that a plastic deformation of the particle takes place.

The element distribution of the milled powders is analyzed by SEM-EDX. The V and Cr are distributed rather uniformly, but Ti looks less homogeneous (fig.7), 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 analyze also reveals the non-uniformity of the Fe that contaminated the milled powders. The EDX results are in concordance with ones obtained by XRD analyses.

Thus, it is clear that mechanical alloying time affects the final particle size and the distribution of elements in the milled powders. 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 contamination.

**Effect of the sintering process**

The MA powder was consolidated by spark plasma sintering at different temperatures and pressures to determine the proper process parameters. The graph representing the sintering process is given in figure 8. A maximum temperature of 1200°C and a force of 12kN were used, with a heating rate of 100°C/min and a holding time of 5 min.

A good compaction is obtained in the SPS process. The theoretical density (TD) of the solid V-4%Cr-4%Ti was assumed to be 6.088g/cm³ and the density obtained for the sintered sample reached over 99.3% TD.

The compact sample composition is determined by XRD analyses. After the sintering process the typical (110) peak of the milled powder shifts to a higher angle (fig. 9). It is possible that the Fe (atomic radius: 0.126nm) dissolved into the V lattice causing lattice shrinkage. The XRD analyses also indicate that during the sintering process some of the vanadium combines with carbon (from the die) to form vanadium carbides and that because V has a very high affinity for C. Therefore, it is necessary to avoid carbon contamination in the SPS process.

The diffraction profile analyses of the compacted samples show that the crystallite size has a small increase.
from 12.7 nm to 14.2 nm (fig. 10), while the maximum strain (fig. 11) touches half of the milled powder strain. Therefore, the SPS process produced relieve of the microstrain in the damaged lattice structure of the mechanically alloyed powders. The EDS mapping for Cr, Ti and Fe distributions in V matrix of the compacted SPS sample is presented in figure 12. The distribution of these elements is clearly shown. The Fe seems to completely dissolve during the SPS process, but Ti still presents high concentration areas.

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 the 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 500 µm for the biggest particles. 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 and an increase in the lattice microstrain induced by ball-powder-ball collision;
- 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/or longer MA time might be necessary to dissolve the Ti particles completely, but this can determine a higher contamination of the alloy during milling;
- stainless steel balls can be incorporated in the V matrix and contaminate the alloy during milling. The contamination can be avoided by adjusting the milling process parameters as rotation speed, milling time, process control agent 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. Also, the Warren-Averbach analyses show the lattice microstrain relieve and a small crystallite size growth in this process.

References

8. ZHENG PF., NAGASAKA T., MUROGA T., CHEN J.M., Microstructures and mechanical properties of mechanically alloyed V-4Cr-4Ti alloy dispersion strengthened by nano-particles, Fusion engineering and Design 89 (2014-1652);
11. VIVES S., GAFFET E., MEUNIER C., X-ray diffraction line profile analysis of iron ball milled powders, Materials Science and Engineering A366, (2004), 229-238;
13. SURYANARAYANA C., Mechanical alloying and milling, Progress in Materials Science 46 (2001), 1-184;

Manuscript received: 12.05.2016