Optimisation of the Chemical Composition and Manufacturing Route for ODS RAF Steels for Fusion Reactor Application

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Abstract. As the upper temperature for use of reduced activation ferritic/martensitic (RAFM) steels is presently limited by a drop in mechanical strength at about 550°C, Europe, Japan and the US are actively researching steels with high strength at higher operating temperatures, mainly using stable oxide dispersion. In addition, the numerous interfaces between matrix and oxide particles are expected to act as sinks for the irradiation-induced defects. Main R&D activities aim at finding a compromise between good tensile and creep strength and sufficient ductility, especially in terms of fracture toughness. Oxide Dispersion Strengthened (ODS) Reduced Activation Ferritic (RAF) steels appear as promising materials for application in fusion power reactors up to about 750°C. Six different ODS RAF steels, with the compositions of Fe-(12-14)Cr-2W-(0.1-0.3-0.5)Ti-0.3Y_2O_3 (in weight percent), were produced by powder metallurgy techniques, including mechanical alloying, canning and degassing of the milled powders, and compaction of the powders by hot isostatic pressing, using various devices and conditions. The materials have been characterized in terms of microstructure and mechanical properties. Results have been analysed in terms of optimal chemical composition and manufacturing conditions.

1. Introduction

Oxide Dispersion Strengthened (ODS) Reduced Activation Ferritic (RAF) steels appear as promising materials for application in fusion power reactors up to about 750°C [1-8]. ODS RAF steels are usually produced by powder metallurgy techniques, including mechanical alloying followed either by Hot Isostatic Pressing (HIPping) or hot extrusion. Processing by mechanical alloying and HIPping usually leads to materials with an isotropic microstructure, and therefore isotropic mechanical properties, but with residual porosity yielding relatively poor Charpy impact properties [9,10]. The Charpy impact behaviour can be eventually improved by means of thermo-mechanical treatments (e.g. forging, hot rolling). Processing by mechanical alloying and hot extrusion usually leads to dense materials with superior Charpy impact properties, but with a non-isotropic microstructure and therefore non-isotropic mechanical properties. This may be improved by applying a recrystallization heat treatment and/or multi-steps cold/hot rolling process.

Despite the large number of published results, there is still a lack of systematic studies comparing the microstructure and mechanical properties of ODS RAF steels with different chemical compositions, produced under various powder metallurgy conditions. This paper presents recent achievements in the manufacture of such materials.

2. Experimental Procedure

Six different ODS RAF steels, with the compositions of Fe-(12-14)Cr-2W-(0.1-0.3-0.5)Ti-0.3Y_2O_3 (in weight percent), were produced by mechanical alloying, canning and degassing of the milled powders, and compaction of the powders by HIPping. Mechanical alloying was performed by milling either elemental Fe, Cr, W, and Ti powder particles (up to 10 μm in size) or pre-alloyed, gas atomised, Fe-14Cr-2W-0.3Ti powder particles (up to 50 μm in size) with 0.3%Y_2O_3 particles (20-30 nm in size). Two types of ball mill have been used, namely a planetary ball mill and a high-energy ball mill, as well as two different milling atmospheres: argon and atmosphere. Various mechanical alloying conditions have been investigated (ball-to-powder ratio (BPR), speed, time, atmosphere) as well as various degassing conditions (temperature, time, vacuum) and HIPping conditions (pressure, temperature, time).

The structure and microstructure of the mechanically alloyed powders and the compacted ingots were characterized by means of X-ray diffractometry (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) equipped with an energy dispersive spectrometry (EDS) system. Chemical analysis of the powders was performed using wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF) as well as LECO TC-436 and LECO IR-412 and LECO-RH-404 analysers for detection of O, N, C and H contents, respectively. The density of the compacted ingots was measured by means of the Archimedes method. The mechanical properties of the compacted ingots were investigated by means of Vickers microhardness measurements, applying a load of 0.98 N for 15 s, Charpy impact tests on V-notch KLST specimens and tensile tests on flat tensile specimens, in an argon flow, using a strain rate of 2×10^{-5} s^{-1}.

3. Results and Discussion

3.1. Mechanically Alloyed Powders

Mechanical alloying device: The as-received powders were mainly composed of round-shape particles. Small and spherical-like particles, homogeneous in size and with a high surface area, are obtained by mechanically alloying elemental powder particles with Y_2O_3 particles in the planetary ball mill, while a bimodal distribution of flake-like particles with a higher microhardness and a lower surface area are obtained by mechanically alloying elemental powder particles with Y_2O_3 particles in the high-energy ball mill, as illustrated in FIG. 1 and Table I in the case of an argon atmosphere.

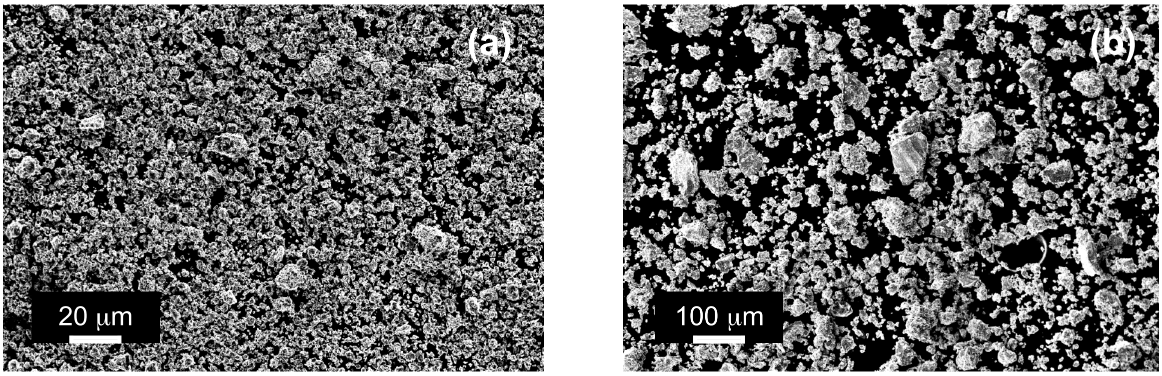

FIG. 1. Morphology of the Fe-14Cr-2W-0.3Ti-0.3Y_2O_3 ODS steel powder particles mechanically alloyed in argon in (a) the planetary ball mill for 45 hrs and (b) the high-energy ball mill for 25 hrs, after [11].

TABLE I: CHARACTERISTICS OF THE Fe-14Cr-2W-0.3Ti-0.3Y_2O_3 ODS STEEL POWDER MECHANICALLY ALLOYED FROM ELEMENTAL POWDERS IN ARGON, IN EITHER THE PLANETARY BALL MILL FOR 45 HRS OR THE HIGH-ENERGY BALL MILL FOR 25 HRS.

Mechanical alloying device	**Surface area [m^2/g]**	**Microhardness [$HV_{0.1}$]**	**Particle size [μm]**	**Sub-grain size [nm]**
Planetary ball mill	0.0801±0.0005	1028±40	46±30	43±15
High-energy ball mill	0.1272±0.0001	825±66	10-100	54±18

Mechanical alloying atmosphere: It has no significant influence on the morphology and size distribution of the ODS steel powder particles. However, the elemental powders mechanically alloyed in a very pure argon atmosphere (99.9999) contain higher oxygen (up to about 0.48 wt.%) and carbon amounts than the powders mechanical alloyed in a pure hydrogen atmosphere (99.999), as reported in Table II. Moreover, after vacuum degassing at temperatures higher than 650°C a much larger loss-of-weight is measured for the powders mechanically alloyed in hydrogen with respect to those mechanically alloyed in argon, as shown in FIG. 2. This is due to reaction of hydrogen with carbon and oxygen present on the surface of the powder particles, during degassing, which yields the production of reduced and then purified particles together with a mixture of CO, CO_2, C_2H_2, and H_2O [12,13].

TABLE II: CHEMICAL COMPOSITION (IN WEIGHT PERCENT) OF THE Fe-14Cr-2W-0.3Ti-0.3Y_2O_3 ODS STEEL POWDER MECHANICALLY ALLOYED FROM ELEMENTAL POWDERS IN THE PLANETARY BALL MILL IN EITHER ARGON OR HYDROGEN.

Atmosphere	C	Si	Cr	W	Ti	Mn	Y	O	N	H
Argon	0.088	0.028	13.7	1.84	0.26	0.18	0.21	0.480	0.190	-
Hydrogen	0.045	0.014	13.7	1.80	0.25	0.10	0.28	0.375	0.057	61.3

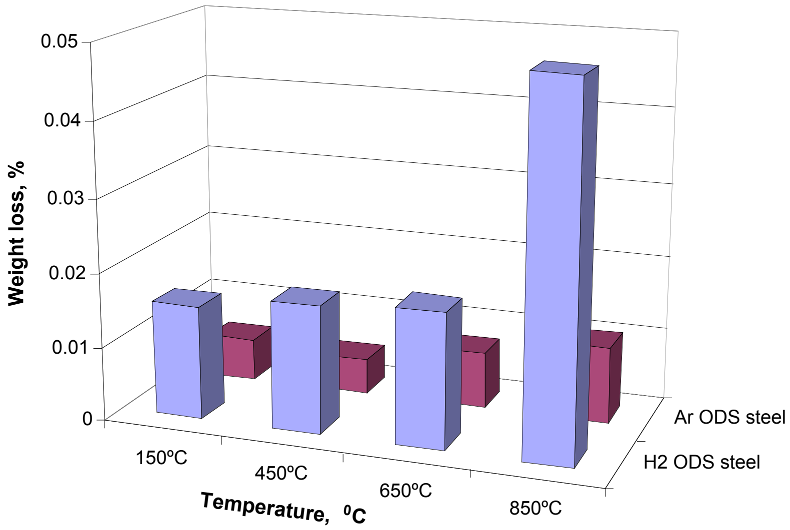

FIG. 2. Loss-of-weight versus degassing temperature for the Fe-14Cr-2W-0.3Ti-0.3Y_2O_3 ODS steel powder mechanically alloyed from elemental powders in either argon or hydrogen, after [14].

Elemental versus pre-alloyed powders: ODS steel powders mechanically alloyed from elemental powders exhibit smaller crystallite and particle sizes and larger lattice strain and microhardness values than ODS steel powders mechanically alloyed using a pre-alloyed powder, while the latter ones contain less oxygen than the former ones, due to the initial lower oxygen content in the pre-alloyed powder.

3.2. Compacted materials

Density: The density of the HIPped ingots clearly increases with compaction pressure, as shown in FIG. 3 in the case of the Fe-14Cr-2W-0.3Ti-0.3Y_2O_3 ODS steel prepared from elemental powders mechanically alloyed in argon. By applying a HIPping pressure of 200 MPa at 1150°C for 3 hrs, it is possible to obtain a density higher than 99% the theoretical one, associated with the presence of residual porosity, however, even applying the above pressure for 5 hrs. By applying a HIPping pressure of 210 MPa at 1150°C for 4 hrs, it is possible to obtain a density (99.8%) very close to the theoretical one. The particle size has no influence on the density of the ingots. A slightly higher density is obtained in the case of elemental powders mechanically alloyed in hydrogen, with respect to argon, as well as when using a pre-alloyed powder instead of elemental powders. A slightly lower density is obtained for 12Cr materials than for 14Cr materials. The various Ti contents have no significant influence on the density of the HIPped ingots. The highest density of 99.9% is obtained as a result of HIPping followed by hot pressing at 850°C, yielding a deformation level of about 50%, and heat treatment at 850°C for 1 hour.

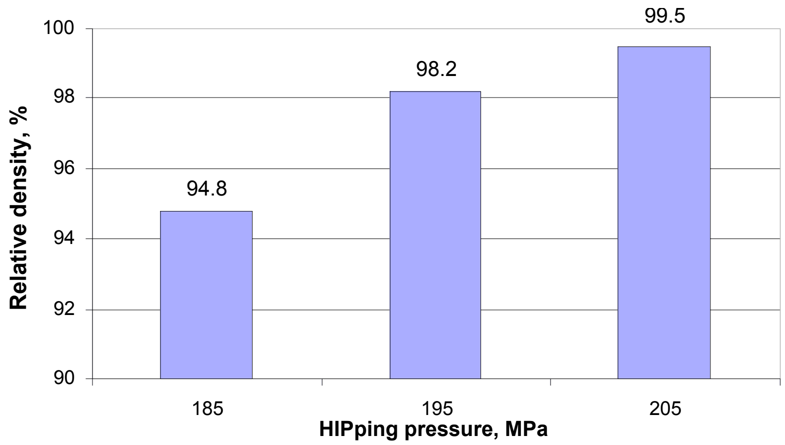

FIG. 3. Relative density versus HIPping pressure for the Fe-14Cr-2W-0.3Ti-0.3Y_2O_3 ODS steel prepared from elemental powders mechanically alloyed in argon and HIPped at 1150°C for 4 hrs.

Microstructure: The compacted materials prepared from elemental powders usually exhibit a fully ferritic (α-Fe, bcc) microstructure with a bimodal distribution of coarse grains, a few micrometres in size, and smaller grains, about 200 nm in size (see FIG. 4a). The coarse grains are almost dislocation-free, while the smaller grains are surrounded by tangles of dislocations. The ingots also contain oxide and carbide impurities (about 100 nm in size) and Y-Ti-O nano-clusters whose size and density decreases, resp. increases, with increasing Ti content (see FIG. 4b). The mechanical alloying atmosphere has no visible effect on the microstructure of the compacted materials. Large TiO_2 particles (50-500 nm in size) are observed in materials containing 0.5%Ti, which may have detrimental effects on the mechanical properties of the ODS RAF steels. 12Cr materials exhibit a microstructure similar to that of 14Cr materials, at least when they are prepared from elemental powders mechanically alloyed in hydrogen. Martensite laths are sometimes observed in 12Cr materials prepared from elemental powders mechanically alloyed in argon, which indicates that these materials are may be less stable than 14Cr materials from the microstructural point of view.

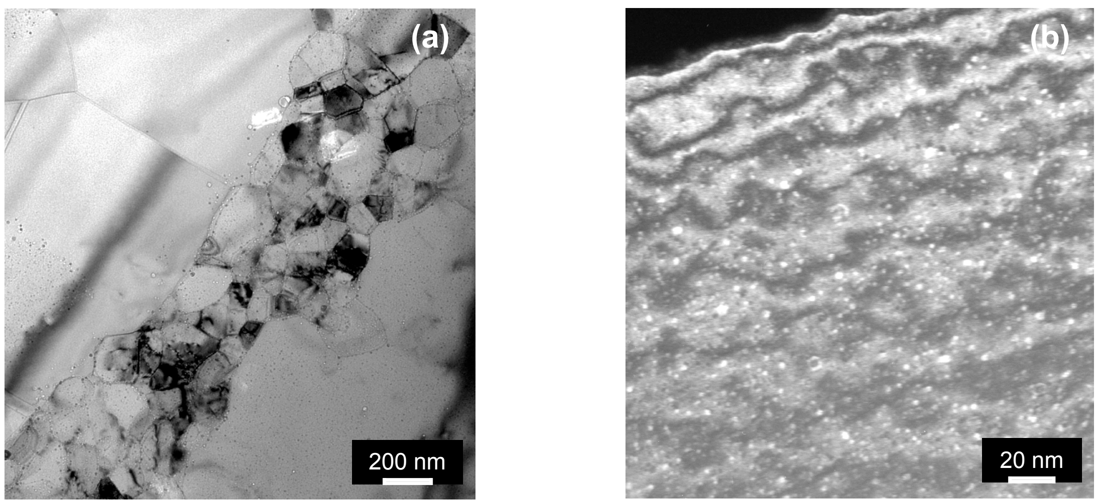

FIG. 4. TEM images of the 14Cr-2W-0.3Ti-0.3Y_2O_3 ODS steel prepared from elemental powders mechanically alloyed in hydrogen: (a) general view, (b) Y-Ti-O nano-clusters, after [10].

The compacted materials prepared using the pre-alloyed powder exhibit a very different microstructure than the ingots prepared from elemental powders, in the sense that they contain equiaxed grains with a mean size of about 10 μm and a higher density of dislocations (see FIG. 5a). They also contain TiO_2 and/or Al_2O_3 particles, with a size in the range 20-100 nm, which appear located preferentially at the grain boundaries (see FIG 5b).

Heat treatment at 850°C for 1 hour has no important effect on the general microstructure of all kinds of produced materials, although a slight increase in the size of the nano-clusters, from about 3 nm to about 8 nm, was sometimes observed, as well as a slight decrease of the dislocation density.

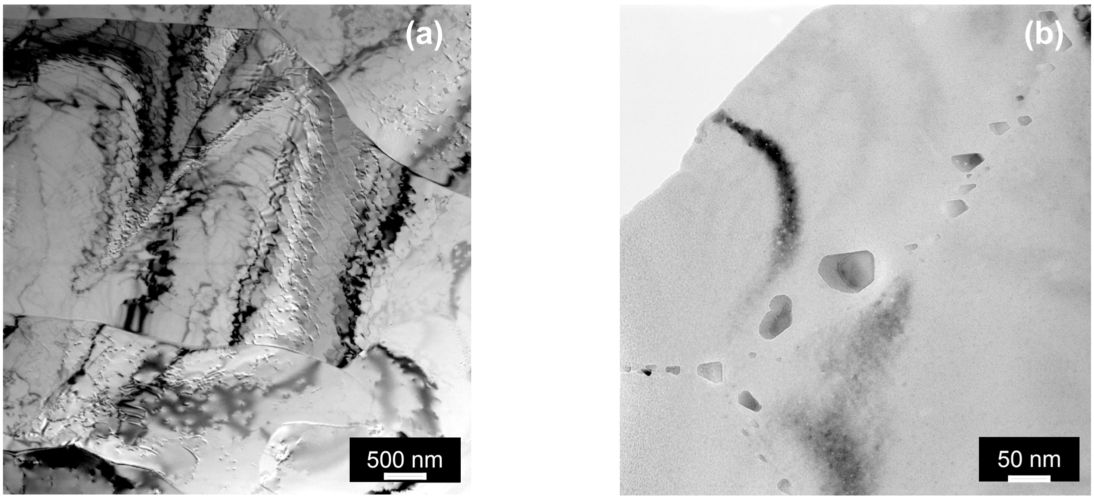

FIG. 5. TEM images of the 14Cr-2W-0.3Ti-0.3Y_2O_3 ODS steel prepared using the pre-alloyed powder mechanically alloyed in hydrogen with Y_2O_3 particles: (a) general view, (b) large oxide impurities.

Microhardness: The compacted materials prepared from elemental powders mechanically alloyed in hydrogen exhibit lower microhardness values than the materials prepared from elemental powders mechanically alloyed in argon (see Table III). The compacted materials prepared using the pre-alloyed powder exhibit higher microhardness values than the materials prepared from elemental powders (see Table III), may be due to the presence of a higher dislocation density in the former ones. Slightly lower microhardness values are obtained for 12Cr materials than for 14Cr materials. The various Ti contents have no significant influence on the microhardness, as well as heat treatment at 850°C for 1 hour (see Table III). However, the microhardness relates to the density in the sense that the lower the density of the ingots the lower the measured microhardness values.

TABLE III: MICROHARDNESS OF HIPPED AND HEAT TREATED (HT) MATERIALS (850°C, 1 H) FOR DIFFERENT MECHANICAL ALLOYING ATMOSPHERES, VARIOUS Cr AND Ti CONTENTS, AND ELEMENTAL VERSUS PRE-ALLOYED POWDERS.

Material	**$HV_{0.1}$**	**$HV_{0.1}$, HT**
Fe-12Cr-2W-0.3Ti-0.3Y_2O_3, elemental powders, hydrogen atmosphere	360±17	346±7
Fe-14Cr-2W-0.1Ti-0.3Y_2O_3, elemental powders, argon atmosphere	381±20	393±23
Fe-14Cr-2W-0.3Ti-0.3Y_2O_3, elemental powders, argon atmosphere	401±19	409±17
Fe-14Cr-2W-0.5Ti-0.3Y_2O_3, elemental powders, argon atmosphere	369±16	372±16
Fe-14Cr-2W-0.3Ti-0.3Y_2O_3, elemental powders, hydrogen atmosphere	369±13	344±14
Fe-14Cr-2W-0.3Ti-0.3Y_2O_3, pre-alloyed powder, hydrogen atmosphere	426±19	414±25

Charpy impact properties: The Charpy impact properties of compacted materials are greatly improved, in terms of upper shelf energy (USE) and ductile-to-brittle transition temperature (DBTT), by the use of a hydrogen atmosphere, instead of argon, during mechanical alloying (see FIG. 6a). For instance, the DBTT of the Fe-14Cr-2W-0.3Ti-0.3Y_2O_3 ODS steel, prepared from elemental powders, is reduced from about 130°C to 20°C, while its upper shelf energy (USE) is increased from about 1.35 to 3.2 J. Weaker Charpy impact properties are obtained when using a pre-alloyed powder instead of elemental powders, due to the numerous oxide particles evidenced in the pre-alloyed powder (see FIG. 6b). The Charpy impact behaviour may be modified by further thermo-mechanical treatments. For instance, hot pressing at 850°C of the Fe-14Cr-2W-0.3Ti-0.3Y_2O_3 ODS steel prepared from elemental powders mechanically alloyed in hydrogen, yielding a deformation level of about 50%, followed by heat treatment at 850°C for 1 h, leads in particular to a strong increase in the USE value, from 3.2 J up to 4.5 J, accompanied by an increase in the DBTT value, from 22°C up to 65°C (see FIG. 6c). The increase in USE may be explained by suppression of the residual porosity, while the increase in DBTT may be due to an increase in dislocation density, which can decrease the dislocation free path, favour stress concentration and thereby cleavage fracture [15,16]. Weaker Charpy impact properties are obtained for 12Cr materials, with respect to 14Cr materials, probably due to the lower density exhibited by the former ones. In what concerns the effect of the Ti content, 0.5%Ti materials seem to exhibit the worse Charpy impact behaviour, especially in terms of USE (see FIG. 6d).

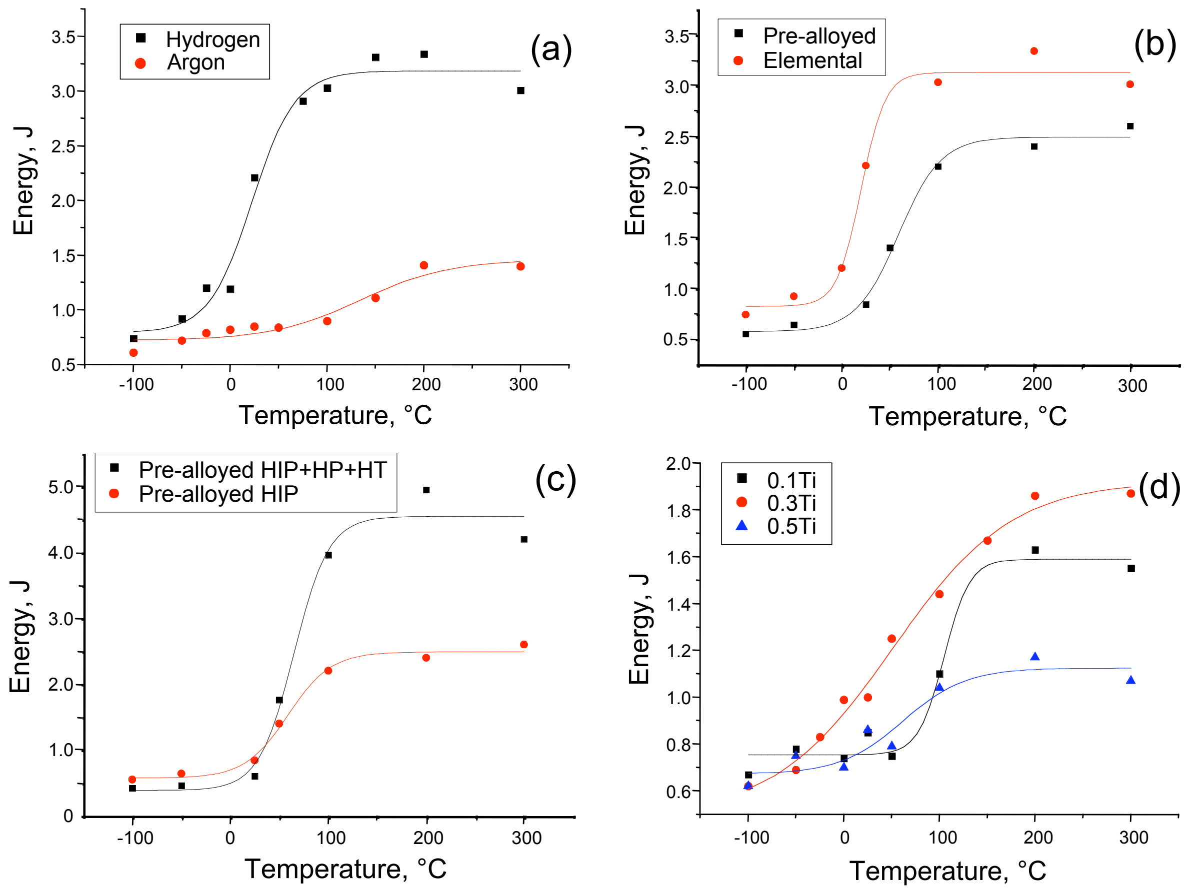

FIG. 6. Absorbed energy versus test temperature for (a) the Fe-14Cr-2W-0.3Ti-0.3Y_2O_3 ODS steel prepared from elemental powders mechanically alloyed in argon or hydrogen, (b) the Fe-14Cr-2W-0.3Ti-0.3Y_2O_3 ODS steel prepared using a pre-alloyed powder or from elemental powders mechanically alloyed in hydrogen, (c) the Fe-14Cr-2W-0.3Ti-0.3Y_2O_3 ODS steel prepared using a pre-alloyed powder mechanically alloyed with Y_2O_3 particles in hydrogen and either HIPped (HIP) or HIPped, hot pressed (HP: 850°C, 50%) and heat treated (HT: 850°C, 1 h), (d) the Fe-12Cr-2W-(0.1-0.3-0.5)Ti-0.3Y_2O_3 ODS steels prepared from elemental powders mechanically alloyed in argon.

<u>Tensile properties:</u> All materials exhibit good tensile strength and elongation values up to about 750°C (see FIG. 7). The Fe-14Cr-2W-0.3Ti-0.3Y_2O_3 ODS steels appears slightly stronger and less ductile in tensile tests than the Fe-12Cr-2W-0.3Ti-0.3Y_2O_3 ODS steels prepared from elemental powders mechanically alloyed in hydrogen. The yield strength (FIG. 7a) and ultimate tensile strength (FIG. 7b) of both materials decrease with raising the test temperature. The uniform elongation (FIG. 7c) of both materials first increases with the test temperature, until it reaches a maximum value at about 300°C, and then decreases with further increasing the test temperature. The total elongation of the 14Cr ODS steels decreases with increasing the test temperature (FIG. 7d). However, the total elongation of the 12Cr ODS steels exhibits a sharp peak at the temperature of about 600°C (FIG. 7d). This may be associated with a dynamic recrystallization phenomenon and/or a change in rate controlling slip system at this temperature [16].

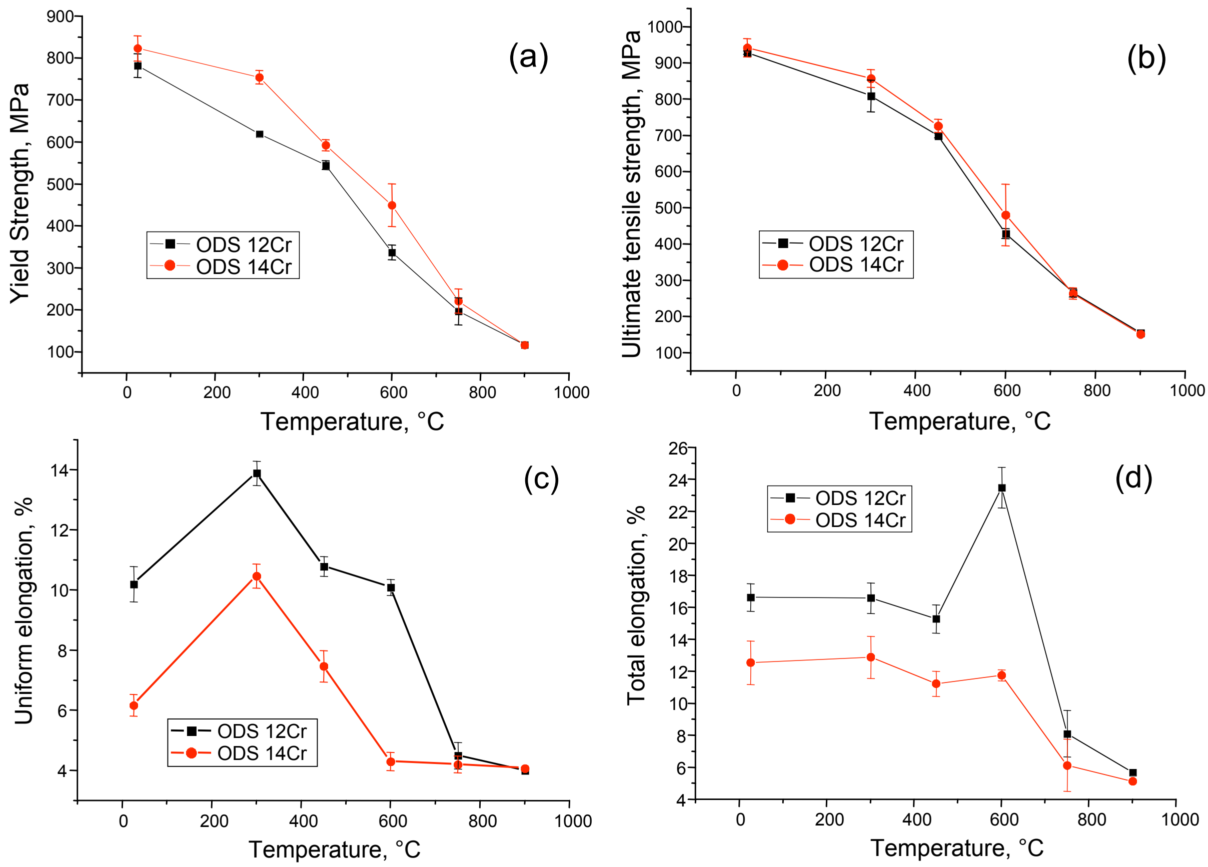

FIG. 7. (a) Yield strength, (b) ultimate tensile strength, (c) uniform elongation, and (d) total elongation of the Fe-(12-14)Cr-2W-0.3Ti-0.3Y_2O_3 ODS steels prepared from elemental powders mechanically alloyed in hydrogen.

4. Conclusions

The main manufacturing conditions for ODS RAF steels are summarized in FIG. 8. Recommendations for the manufacturing process of ODS RAF steels are the following: (1) planetary ball milling is preferred over high-energy ball milling; (2) hydrogen should be used as mechanical alloying atmosphere; (3) a high degassing temperature (≥ 925 K) should be applied to the mechanically alloyed powders; (4) the composition of the materials should lie in the range Fe-14Cr-2W-(0.3-0.4)Ti-(0.25-0.3)Y_2O_3, as 14Cr ODS RAF steels exhibit higher tensile strength and better Charpy impact properties, and they are more stable than 12Cr materials (no risk of martensitic transformation); (5) materials with 0.5%Ti or more should not be further investigated, due to potential embrittlement by large TiO_2 particles.

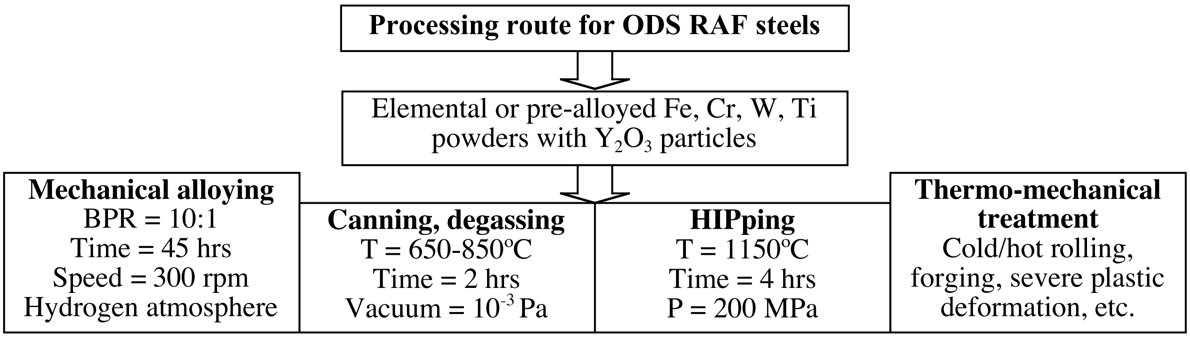

FIG. 8. Main manufacturing conditions for ODS RAF steels.

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References

[1] LINDAU, R., et al., “Present development status of EUROFER and ODS-EUROFER for application in blanket concepts”, Fusion Engng Design **75–79** (2005) 989–996.
[2] BALUC, N., et al., “On the potentiality of using ferritic/martensitic steels as structural materials for fusion reactors”, Nucl. Fusion **44** (2004) 56-61.
[3] KLUEH, R.L., et al., “Oxide dispersion-strengthened steels: A comparison of some commercial and experimental alloys”, J Nucl. Mater. **341** (2005) 103-114.
[4] MILLER, M.K., et al., “Characterisation of precipitates in MA/ODS ferritic alloys”, J. Nucl. Mater. **351** (2006) 261-268.
[5] MONNET, I., “Microstructural investigation of the stability under irradiation of oxide dispersion strengthened ferritic steels”, J Nucl. Mater. **335** (2004) 311-321.
[6] YOSHITAKE, T., et al., “Ring-tensile properties of irradiated oxide dispersion strengthened ferritic/martensitic steel claddings”, J Nucl. Mater. **329-333** (2004) 342-346.
[7] KLUEH, R.L., et al., “Tensile and creep properties of an oxide dispersion-strengthened ferritic steel”, J Nucl. Mater. **307-311** (2002) 773-777.
[8] KIM, I-S., et al., ISIJ International, **43** (2003) 1640-1646.
[9] UKAI, S., et al., “Perspective of ODS alloys application in nuclear environments”, J. Nucl. Mater. **307-311** (2002) 749-757.
[10] OKSIUTA, Z., BALUC, N., “Microstructure and Charpy impact properties of 12-14Cr oxide dispersion-strengthened ferritic steels”, J Nucl. Mater. **374** (2008) 178-184.
[11] OKSIUTA, Z., BALUC, N., “Microstructural characterization of an oxide dispersion strengthened ferritic steel powder prepared by mechanical alloying in two different ball mills”, submitted for publication in Fusion Engng Design.
[12] IACOVIELLO, F., et al., “Sintered stainless steel: Fatigue crack propagation resistant under hydrogen charging conditions”, Corrosion Science **49** (2007) 2099-2117.
[13] LARSEN, K.A., et al., “Mechanical properties of metal injection moulded 316l stainless steel using both prealloy and master alloy techniques”, Powder Metallurgy **37** (1994) 61-66.
[14] OKSIUTA, Z., BALUC, N., “Effect of mechanical alloying atmosphere on the microstructure and Charpy impact properties of an ODS ferritic steel”, submitted for publication in J. Nucl. Mater.
[15] COURTNEY, T.C., Mechanical Behaviour of Materials, McGraw-Hill International Edition, Second Edition, Boston (2000).
[16] DIETER, G.E., “Mechanical Metallurgy”, McGraw-Hill Book Company, London, 1988.