

ANALYSIS OF METALLIC MATERIALS FOR ITER WITH THE EMPHASIS ON COPPER ALLOYS

Tibor Kvačkaj^{1)*}, Róbert Bidulský¹⁾, Andrea Kováčová¹⁾, Jana Ileninová¹⁾, Jana Bidulská¹⁾

¹⁾ Technical University of Košice, Faculty of Metallurgy, Košice, Slovakia

Received: 02.10.2014

Accepted: 28.11.2014

*Corresponding author: *e-mail: tiber.kvackaj@tuke.sk Tel.: +421 55 602 4259, Department of Metal Forming, Faculty of Metallurgy, Technical University of Košice, Vysokoškolská 4, 042 00 Košice, Slovakia*

Abstract

The production of electrical energy from nuclear fusions is currently highly advanced field of the interest in an international scientific cooperation in the International Thermonuclear Experimental Reactor programme (ITER). Alloys based on Cu are used in the ITER project however from the future perspective in terms of the physical and mechanical properties improvement, the alloy based on CuCrZr is proposed. The CuCrZr alloy is classified as a precipitation-hardened material which is used as a functional material for various applications in ITER, for example the first wall, blanket and support, divertor and heating systems. In this study, as an experimental material was used CuCrZr alloy with the chemical composition of 98.54 wt.% Cu, 1.1 wt.% Cr, 0.043 wt.% Zr and 0.317 wt.% impurities. There was used ECAP method and heat treatment to enhance the strength properties in CuCrZr alloy. The application of sophisticated treatments based on solution annealing, structure formation by ECAP on nano-scale level and additional artificial ageing producing precipitation strengthening can be achieved the yield strength more than 500MPa.

Keywords: CuCrZr alloys, equal channel angular pressing, heat treatment, International Thermonuclear Experimental Reactor

1 Introduction

According to the OECD, the world-wide consumption of energy will be still increasing in the following 20-60 years, moreover mostly in the field of energy generated from „pure sources“ [1]. As „pure sources“ there are considered pure fossils, renewable resources and nuclear fusion. Progress in the application of pure energetic sources is suppose that in 2050 (as predicted by the OECD Green Model [1]) a break point will be reached and consequently afterwards pure energetic sources based on nuclear fusion will be crucial. Considering suitability of the energy transformation on the electrical energy and ability to produce the energy in a huge volume not depending on the external restrictions, primary sources based on nuclear fusion provide the best alternative to all others. The planned world-wide consumption in electrical energy is expected to increase the electric power from 19 TWh in 2011 to 35 TWh in 2035. A long-term prediction of the electrical energy consumption is expected the increasing in electric powers as follows: 44 TWh in 2045 and 100 TWh in 2080[2].

According to the above mentioned prognoses and analyses, there is obvious that the production of electrical energy from nuclear fusion reactor which are currently highly advanced field of the interest in an international scientific cooperation in the ITER (International Thermonuclear Experimental Reactor) programme will be increasing to the end of the 21st century. Countries as

EU, USA, Russia, China, Japan, South Korea and India have been involved in the project, with the prospective to join the Brazil. Fusion technology programme ITER will be progressing in the following projects: Demonstration Reactor (DEMO) and Commercial Fusion Reactor (CFR).

From the structural materials point of view, ITER is a low temperature reactor (<300°C), for DEMO is supposed rising of temperature reactor (EU design 250-550°C) and for CFR is supposed an even higher temperature reactor ($\geq 550^\circ\text{C}$) [3]. For all these reactors is requested the availability of materials to resist the severe thermo-mechanical loadings and irradiation damage.

According to author [4-6] following materials are very popular:

- a) Steels: Stainless steel type 316LN-IG for ITER, used in the structural components (vacuum vessel, back-plate, manifolds, shield, divertor cassette body and other), Martensitic steel type T91, modified 9Cr1-Mo, F82H steel low activation grades of which are developed for the structural components of DEMO, Fe-Y₂O₃.
- b) Nonferrous metals: Copper alloys CuCrZr, DS-Cu (heat sink and divertor), Aluminum alloys (AW2014, AW2024, AW6061), Titanium alloys, Nickel base alloys, Superalloys Hastalloys, Vanadium alloys, Molybdenum alloys, Niobium alloys, Tantalum alloys, Tungsten alloys.

The materials for ITER and DEMO are operated for the following temperature conditions:

- a) Metal materials operated at cryogenic temperatures: cryoplant, transport systems and cryostat vessel. All these users require helium cryogen at different temperature levels ranging from 4.5 K to 50 K and up to 80 K and pressure 0.4 MPa [7].
- b) Metal materials operated at high temperatures (300-700°C) which are assigned for first wall and blanket components of reactor [4].

The first nuclear reactor (power 500-700 MW) is currently in the process of building near to Marseille in the Cadarache and it would become the second most expensive scientific-technical centre in the world, after the ISS space station [8].

2 Materials and components for ITER

In original strategy of the ITER project, selected metallic materials used for various constructive components were being considered as commercial and industrial - manufactured materials. Initial highly-promising results coming from the ITER project have provided the development of new, metallic materials as well, while standards on material properties will be reflection to previous experiences of international scientific institutions across the world. Types of materials used for the several ITER components are given in **Table 1** [9] and in **Table 2** [10], there are presented metallic materials mostly applied in fusion reactors.

The development of metallic materials which are used as constructive components is under significant world-wide consideration as a result a lot of international scientific meetings and workshops with such objective have been organized in last years [11].

Alloys based on Cu have been involved in the ITER project however from the future perspective in terms of the physical and mechanical properties improvement through the opportunity to form the microstructure in a nano-scale range, the alloy based on CuCrZr is proposed.

3 CuCrZr alloys

The CuCrZr alloy is classified as a precipitation - hardened (PH) material processed by heat treatment. Typical heat treatment is based on solution annealing at high temperatures followed by water quenching (WQ) in order to create a supersaturated solid solution and ageing. The ageing process produces fine precipitates of the second phase with a precipitation hardening

Table 1 Materials for the several ITER components [9]

Material	Forms	Material	Forms
Thermal shield		First wall	
Steel 304L	Plates, tubes	Beryllium (S-65C or equivalent)	Armor tiles
Ti-6Al-4V	Plates	CuCrZr	Plates/cast/powder heart sink
Steel grade 660	Fasteners	316L(N)-IG	Plates, pipes
Alloy 718	Bolts	Blanket and support	
Al ₂ O ₃ coatings	Plasma sprayed insulation	316L(N)-IG	Plates, forgings, pipes Cast, powder HIP
Glass epoxy G10	Insulation	Ti-6Al-4V	Flexible support
Ag coating	Coating, 5 μm (emissivity)	CuCrZr	Sheets
Vacuum vessel and ports		Alloy 718	Bolts
Steel 316L(N)-IG	Plates, forgings, pipes	NiAl bronze	Plates
Steel 304	Plates	Al ₂ O ₃ coatings	Plasma sprayed insulation
Steel 660	Fasteners, forgings	CuNiBe or DS Cu	Collar
Ferritic steel 430	Plates	Divertor	
Borated steels 304B7 and 304B4	Plates	CFC (NB31 or equivalent)	Armor tiles
Alloy 718	Bolts	W	Armor tiles
Steel 316 (B8M)	Bolts	CuCrZr	Tubes, plates
Steel XM-19 (B8R)	Bolts	316L(N)-IG	Plates, forgings, tubes
Pure Cu	Clad	Steel 660	Plates, bolts
VV support		Steel XM-19	Plates, forgings
Steel 304	Plates, rods	Alloy 718	Plates
Steel 660	Fasteners	NiAl bronze	Plates, rods
Alloy 718	Bolts		
NiAl bronze	Rods		
PTFE	Plates		

effect. Such alloys provide high mechanical properties, high heat resistance, high electrical and thermal conductivity [3]. The mechanical properties of PH alloys depend strongly on following strengthening mechanisms: grain refinement (up to a nano-scale level), precipitation hardening through the presence of second phase particles, dislocation hardening, solid solution and Peierls-Nabarro hardening. Nowadays, equal channel angular pressing (ECAP) is a method based on severe plastic deformation (SPD) which has been successfully used for reducing the grain size diameter and to increase the dislocation density resulting in greater mechanical properties [12-14]. The post-processing after ECAP through the ageing process (temperature vs. time conditions) has an impact on final mechanical properties by the effect of precipitation hardening [15, 16]. To obtain the precipitation hardening effect there is necessary to apply the solution annealing (SA) followed by WQ in order to dissolve the second phase particles in the solid

solution. Further ECAP processing leads to the structural refinement and together with combination of the post ECAP ageing to the precipitation strengthening what finally has an impact on the mechanical properties increasing. The effect of precipitation strengthening depends on the amount of a Cr and a Zr content that can be in the range of $Cr \in <0.4; 1.5>$ [wt.%] and $Zr \in <0.03; 0.5>$ [wt.%]. Authors [17] have mentioned that the Zr content can also be reduced to 0.1 wt.% or less. According to the authors [18], an average solubility of the concentration for chromium is $Cr_{Solubility} \approx 0.4$ wt.% at $1000^{\circ}C$ on the other hand when temperature falls down at $400^{\circ}C$, an average solubility of the concentration is dramatically changed to $Cr_{Solubility} \approx 0.03$ wt.%. Since low content of Cr provides the coarse Cr precipitates forming, tendency is to obtain the Cr content below upper limit.

Table 2 Selected materials in the ITER reactor [10]

Material	Material Grade	Components
Armour		
Beryllium	S-65C VHP or equivalent	Armour for first wall and limiter
Tungsten	Pure W	Armour for divertor
CFC	SEP NB 31 or equivalent	Armour for divertor
Structural		
Austenitic steels	316L(N)-IG	Blanket shield modules Thin walled pipes Cooling manifolds Divertor body
	304L, 316L	Cooling pipes
	XM-19	Divertor support
PH steel	Steel grade 660	Divertor support
Cu alloys	CuCrZr	PFCs, heating systems, electrical strips, etc.
	NiAl bronze	Divertor attachment
	CuNiBe	Support system
	DS Cu	Heating systems
Functional		
Austenitic steel	316	Fastening components
PH steel	Steel grade 660	Fastening components
Ni alloys	Alloy 718	Bolts Divertor connections
Ti alloy	Ti-6Al-4V	Blanket attachment
Ceramic	Al_2O_3 or $MgAl_2O_4$	Electrical insulators
Special materials		Pure Cu Pure Ni Low C iron Brazes Weld fillers

The summary of chemical composition resulting from the literature study is given in **Table 3**.

Table 3 Summary of chemical composition [wt.%]

Alloy Designation	Cu	Cr	Zr	Other elements	O ₂
CuCrZr	base	0.4-1.5	0.03-0.5	0.01 max (0.05 Cd)	0.002max

Considering precipitation processes, in literature there are a lot experimental studies mostly carried out under following conditions: $T_{SA} \in (950; 970) [^{\circ}\text{C}]$, $t_{SA} \in <0.3; 3> [\text{h}]$ + WQ followed by cold rolling or tensile testing with subsequent ageing treatment at $T_{AT} \in <400; 525> [^{\circ}\text{C}]$, $t_{AT} \in <0; 20> [\text{h}]$ [19-24]. In these studies, there have been not documented presence of any intermetallic chromium or zirconium phases in the microstructure, only presence of Cr precipitates together with coarse Cu_5Zr or Cu_3Zr in its surrounding embedded in to a pure Cu matrix. The precipitation temperature was determined at $T \sim 370^{\circ}\text{C}$ and $\text{Cr } T \sim 425^{\circ}\text{C}$ for Cu_5Zr or Cu_3Zr and Cr (with a diameter of 1-50nm), respectively. Hence, according to the literature overview, there is necessary to perform additional experimental studies.

On the previous analysis was made the summary of treatment conditions on material properties which are given in **Table 4**.

Table 4 The analysis treatment conditions with relationship to precipitation of CuCrZr alloys

No.	Solution annealing	Deformations	Post deformation treatment	Precipitates	Ref.
1.	950°C/2h+WQ	Cold rolling	450°C/2h	Cu matrix+Cr phase+Zr phase No intermetallic	[19]
2.	960°C/3h+WQ	Tensile test	460°C/3h	Fine Cr +small density of Zr precipitates	[20]
3.	970°C/20min+WQ	Cold rolling	425°C/3h 475°C/3h 525°C/3h	Cr precipitates around a core of or Cu_5Zr embedded in a pure Cu matrix	[21]
4.	980°C/2h+WQ	-	450°C/20h	Coarse precipitates are pure Cr and Cu_5Zr , the dispersed fine precipitates of $\text{CrCu}_2(\text{Zr},\text{Mg})$ and pure $\text{Cr} \in <1;50> [\text{nm}]$. Coarse phases formed during solidification and were left undissolved during solution annealing.	[22]
5.	Sample was jetted under the pressure of pure Ar to acopper roller rotating	-	$T_{\text{ageing}} \in <400; 480> [^{\circ}\text{C}]$ $t_{\text{ageing}} \in <0; 3> [\text{h}]$	Cu matrix + Cr + Cu_5Zr	[23]
6.	950°C+WQ	Cold rolled $\varepsilon=83\%$	400°C, 450°C, $t_{\text{ageing}} \in <5;100> [\text{min}]$	Without of deformation: the Cr at 440°C and + Cu_3Zr at 520°C. Cold rolling: Cu_3Zr at 370°C + Cr at 425°C	[24]

7.	1000°C/1h+WQ	-hydrostatic extrusion: $\phi=3,77$ - 8xECAP: $\phi=11,5$	-	-	[25]
Σ	$T_{SA} \in (950; 970) [^{\circ}\text{C}]$ $t_{SA} \in <0.3; 3> [h]$ +WQ	-Cold rolling -Tensile test -Hydrostatic extrusion -SPD	$T_{AT} \in <400; 525> [^{\circ}\text{C}]$ $t_{AT} \in <0; 20> [h]$	Cu matrix + (Cr + Cu ₅ Zr/Cu ₃ Zr) precipitates $D_{\text{particles}} \in (0; 50) [nm]$	
The literature overviews about precipitation have not uniform conclusion.					

4 Experimental material and methodics

As an experimental material, CuCrZr alloy in a cylindrical bar ($D \times L = 10 \times 100$ mm) with the chemical composition of 98.54 wt.% Cu, 1.1 wt.% Cr, 0.043 wt.% Zr and 0.317 wt.% impurities was used. Before ECAP, samples were heat treated under following conditions: $T_{SA} = 1020^{\circ}\text{C}$, $t_{SA} = 1\text{h} + \text{WQ}$. The samples were processed once through an ECAP die (channel's angle $\Phi = 90^{\circ}$, $\Psi = 32^{\circ}$ and the diameter of 10 mm) at ambient temperature, with route Bc.

The samples after one ECAP pass were aged under following conditions: $T_{AT} \in (20; 480) [^{\circ}\text{C}]$, $t_{AT} \in <30; 150> [\text{min}]$ followed by cooling in water. The static tensile tests were carried out according to a STN EN 10002-1 standard by Tinius Olsen machine.

5 Result overview

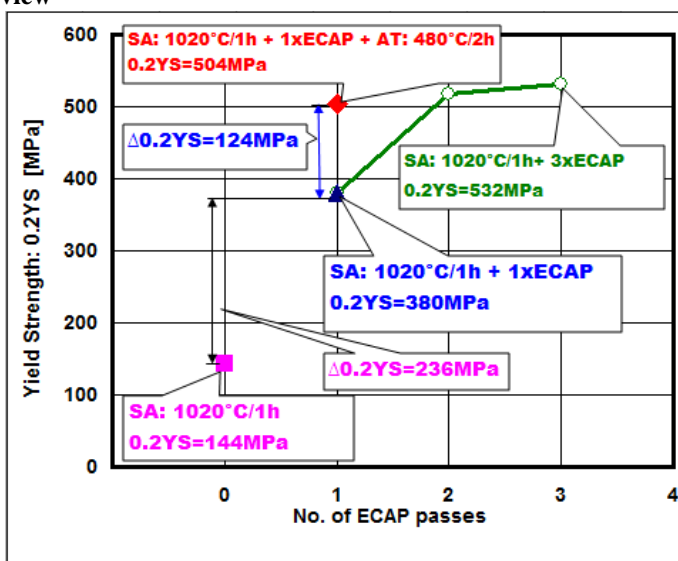


Fig. 1 The strength analysis after some treatment stages (a:SA+1xECAP+AT, b:SA+3xECAP)

The strength analysis after some treatment stages is given in Fig.1 from which is resulting that after application only SA yield strength was very small 0.2 YS = 144 MPa. The sample processing by one ECAP pass increased the yield strength level up 0.2 YS = 380 MPa what is

representing the increment $\Delta 0.2 \text{ YS} = 246 \text{ MPa}$. This increment is achieved by effect from grain size refinement. The diameter of grain size before ECAP was $40 \mu\text{m}$ and after one ECAP pass was reduced on $0.5 \mu\text{m}$. If samples after processing by SA+1xECAP were treated by ageing regime ($480^\circ\text{C}/2\text{h}$) the yield strength was increase on level $0.2 \text{ YS} = 504 \text{ MPa}$ what is representing the increment $\Delta 0.2 \text{ YS} = 124 \text{ MPa}$ with comparison of state after 1xECAP. This increment is achieved by effect obtained from precipitation hardening. On the other hand this strength level is possible to obtain also by structure refinement via 3xECAP which produced diameter of grain size $0.5 \mu\text{m}$ and $0.2 \text{ YS} = 532 \text{ MPa}$. The increment $0.2 \text{ YS} = 152 \text{ MPa}$ was achieved by effect from grain size refinement with comparison to state SA+1xECAP.

6 Conclusions

In the present study, there is used ECAP method and heat treatment to enhance the strength properties in CuCrZr alloy.

According to this study, following conclusions can be made:

- on the essential electricity consumption prognosis for to 21 century should be assumed that in 2080 year will be necessary reach electricity power 100TWh,
- this electricity power will be achieve by „pure sources“ there are considered pure fossils, renewable resources and nuclear fusion,
- the very effective and perspective pure source is appears nuclear fusion,
- nuclear fusion is running in thermonuclear reactor for which must be selected special grades of metal materials,
- one special grades of metal material is precipitation hardening CuCrZr alloy,
- today research orientation is preparing processing conditions leading to maximalization of strength properties and weight reducing of construction elements,
- by sophisticated treatment of CuCrZr alloy was obtained yield strength $0.2\text{YS} > 500 \text{ MPa}$,
- sophisticated treatments are based on two lines:
 - SA+1xECAP+AT=144MPa (base level) + 236MPa (effect from grain size refinement) + 124MPa (effect from precipitation hardening) = 504 MPa,
 - SA+3xECAP=144MPa (base level) + 388MPa (effect from grain size refinement)=532 MPa.

References

- [1] World Energy Statistics and Balances of OECD Countries, International Energy Agency, www.iea.org, 2014
- [2] OECD/EA World Energy Outlook 2009
- [3] A.A.F. Tavassoli: Journal of Nuclear Materials, Vol. 258-263, 1998, No. 1A, p. 85-96
- [4] A.A.F. Tavassoli: Journal of Nuclear Materials. Vol. 302, 2002, No. 2-3, p. 73-88, DOI:10.1016/S0022-3115(02)00794-8
- [5] T. Muroga: Materials Transactions, Vol. 46, 2005, No. 3, p. 405-411, DOI:10.2320/matertrans.46.405
- [6] S. Wang et al.: Journal of Nuclear Materials, Vol. 455, 2014, No. 1-3, p.174-179, DOI: 10.1016/j.jnucmat.2014.05.073
- [7] B. Doshi et al.: Fusion Engineering and Design, Vol. 86, 2011, No. 9-11, p. 1924-1927, DOI:10.1016/j.fusengdes.2011.01.037
- [8] P. Thomas: *Technical Status of the ITER Project*, Budker Institute, 2014
- [9] *ITER Materials Properties Handbook* (MPH), ITER Doc. G 74 MA 16 04-05-07 R0.1

- [10] V.R. Barabash et al.: *ITER Materials*, ICFRM-12, 2005, Santa Barbara, USA, unpublished
- [11] *ICFRM – International Conference on Fusion Reactor Materials*, International Conference Nuclear Energy for New Europe, 2014
- [12] T. Kvačkaj et al.: *Micron*, Vol. 43, 2012, No. 6, p. 702-724, DOI: 10.1016/j.micron.2012.01.003
- [13] T. Kvačkaj et al.: *Materials Letters*, Vol. 64, 2010, No. 21, p. 2344-2346, DOI: 10.1016/j.matlet.2010.07.047
- [14] R. Bidulský, J. Bidulská, M. Actis Grande: *High Temperature Materials and Processes*, Vol. 28, 2009, No. 5, p. 337-342
- [15] T. Kvačkaj, J. Bidulská: *Materials Science Forum*, Vol. 783-786, 2014, p. 842-847, DOI: 10.4028/www.scientific.net/MSF.783-786.842
- [16] M. Matvija et al.: *Acta Metallurgica Slovaca*, Vol. 18, 2012, No. 1, p. 4-12
- [17] D.L. Ellis, B.A. Lerch: *Improvement of GRCo-84 through the Addition of Zirconium*. NASA Technical Reports, Report/Patent Number: NASA/TM-2012-216985, E-17626, 2012
- [18] H. Fuxiang et al.: *Scripta Materialia*, Vol. 48, 2003, No. 1, p. 97-102, DOI:10.1016/S1359-6462(02)00353-6
- [19] V.R. Barabash, G.M. Kalinin, S.A. Fabritsiev, S.J. Zinkle: *Journal of Nuclear Materials*, Vol. 417, 2011, No. 1-3, p. 904-907, DOI: 10.1016/j.jnucmat.2010.12.158
- [20] M. Hatakeyama et al.: *Materials Transactions*, Vol. 49, 2008, No. 3, p. 518-521, DOI: 10.2320/matertrans.MBW200736
- [21] U. Holzwarth, M. Pisoni, R. Scholz, H. Stamm, A. Volcan: *Journal of Nuclear Materials*, Vol. 279, 2000, No. 1, p. 19-30, DOI: 10.1016/S0022-3115(99)00278-0
- [22] Z. Mei, L. Guobiao, W. Zidong, Z. Maokui: *China Foundry*, Vol. 5, 2008, No. 4, p. 268-271
- [23] Z. Pan, J. Chen, W. Zhou, J. Li: *Materials Transactions*, Vol. 54, 2013, No. 8, p. 1403-1407
- [24] H. Suzuki, M. Kanno: *Journal of the Japan Institute of Metals and Materials*, Vol. 36, 1972, p. 363-368 (in Japanese)
- [25] M. Verdier et al.: *Scripta Materialia*, Vol. 37, 1997, No. 4, p. 449-454

Acknowledgements

This work was financially supported by the VEGA 1/0325/14 project.