ELSEVIER

Journal of Nuclear Materials 283–287 (2000) 597–601

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Thermomechanical characteristics of the low activation materials chromium and Cr·5Fe·1Y_2O_3 alloy

H. Stamm [a,*], U. Holzwarth [a], F. Lakestani [a], R. Valiev [b], V. Provenzano [c], A. Volcan [a]

[a] *European Commission, Joint Research Centre, Institute for Health and Consumer Protection, Via Fermi n°1, Ed. 20i, T.P. 202, I-21020 Ispra, Italy*

[b] *Institute for Physics of Advanced Materials, Ufa State Aviation Technical University, Ufa 450000, Russian Federation*

[c] *Naval Research Laboratory, Washington DC 20375-5343, USA*

Abstract

Recent results of studies of basic physical and mechanical properties of sintered high purity chromium and a sintered Cr · 5Fe · 1Y_2O_3 alloy are presented. The materials were investigated in the temperature range from room temperature to 900°C and characterized by tensile testing, measurements of thermal diffusivity, thermal expansion, and heat capacity, complemented by metallography and fractography. The results are discussed with regard to transient thermal loading faced by first wall structures. In order to overcome the problem of brittleness and lack of ductility at low temperatures, preliminary results on the effect of microstructure refinement by severe plastic deformation are presented. These results indicate that the strength of pure chromium can be appreciably increased, and the brittleness may be reduced.

1. Introduction

The main attraction of chromium and chromium alloys as potential structural material in fusion reactors arises from their excellent low activation properties and their potential high service temperature of up to 1000 K [1,2]. Recent investigations have shown that the commercially available high purity chromium (DUCROPUR™) [1] and the alloy Cr · 5Fe · 1Y_2O_3 show excellent low activation characteristics [1]. The first wall made of DUCROPUR may be classified as 'low level waste' after 50 years of cooling [1]. Neither SiC/SiC composites nor V–5Ti fall into this classification, and the superiority of pure chromium and Cr · 5Fe · 1Y_2O_3 may even be improved by a further reduction of Mo impurities [1].

Chromium alloys have been studied in the 1950s and 1960s for high temperature applications in jet engines [3,4]. Although, chromium alloys exhibit a favourable strength to density ratio combined with a high elastic modulus and melting point, the nitrogen embrittlement and the high ductile to brittle transition temperature gave preference to nickel-based superalloys.

The required low activation behaviour and the necessity to withstand severe cyclic thermal loading in fusion reactors have again drawn attention to chromium alloys. Their high thermal conductivity, along with a low thermal expansion coefficient, yields lower thermal stresses during transient thermal loading as compared to steels and other materials [2,5]. In the present paper, the thermomechanical properties of the above-mentioned materials are discussed and first results of attempts to increase the low temperature ductility by nanostructuring using severe plastic torsional deformation [6,7] are presented.

2. Materials and test methods

The materials investigated were the commercially available 99.7% pure chromium (DUCROPUR™) and

* Corresponding author. Tel.: +39-0332 789 030; fax: +39-0332 785 388.

E-mail address: hermann.stamm@jrc.it (H. Stamm).

[1] Trademark of Metallwerke Plansee AG, Austria.

0022-3115/00/$ - see front matter
PII: S0022-3115(00)00110-0

Table 1
Chemical composition of the investigated materials (all values in wt% or ppm)

Element	O	N	H	C	Fe	Y	Al	Mo
Cr 99.7%	<0.01	<0.005	<0.0005	<0.01	<0.25	–	<0.001	<0.0002
Cr 5Fe $1Y_2O_3$	0.43	115 ppm	5 ppm	15 ppm	5.3	0.68	–	<0.0002

the dispersion hardened sintered alloy $Cr \cdot 5Fe \cdot 1Y_2O_3$. The chemical compositions are compiled in Table 1. The grain size of 82 μm in DUCROPUR and 11 μm in $Cr \cdot 5Fe \cdot 1Y_2O_3$ was determined after electrolytic etching using the lineal intercept method.

The laser flash method [8] has been used to determine the thermal diffusivity between room temperature and 1000°C. Specimens of 1.5 mm thickness were heated on one side by a short laser pulse. The temperature increase was detected on the opposite side and the thermal diffusivity was determined from the characteristics of the recorded temperature transient.

The heat capacity was measured in a differential scanning calorimeter, using slabs of 1 mm thickness and 6 mm diameter with reference to a sapphire sample and to an empty platinum crucible. The measurements were performed in the temperature range between 50°C and 1000°C in an argon atmosphere with a heating rate of 20 K/min.

The thermal expansion was measured on cylinders of 6 mm diameter and 25 mm length with reference to an Al_2O_3 specimen with identical dimensions.

Displacement controlled tests were performed in air at temperatures between 20°C and 900°C using electromechanical testing machines. Flat specimens with cross-sections of 4×1 mm and round specimens with a diameter of 4 mm in the gauge length were tested with different cross-head velocities.

Torsional straining under high quasi-isostatic pressure was applied to introduce an ultra-fine grained structure by formation of subgrains with high angle grain boundaries. Billets of DUCROPUR and $Cr \cdot 5Fe \cdot 1Y_2O_3$ were subjected to an isostatic pressure of up to 6 GPa placing them between a fixed lower anvil and a rotating upper anvil [6]. Up to 5 complete turns of the anvil were performed at 400–600°C due to the limited ductility at room temperature.

3. Results

3.1. Physical properties

Fig. 1 illustrates that pure Cr has a significantly higher thermal diffusivity μ than the $Cr \cdot 5Fe \cdot 1Y_2O_3$ alloy.

From Fig. 2 it is obvious that the temperature dependence of the heat capacity $c(T)$ of DUCROPUR and $Cr \cdot 5Fe \cdot 1Y_2O_3$ are nearly identical and show an approximately linear increase between 50°C and 1000°C. The figure also shows the measured temperature dependence of the average thermal expansion coefficient α_m. The typical values for DUCROPUR and $Cr \cdot 5Fe \cdot 1Y_2O_3$ between 8×10^{-6} and 11×10^{-6} K^{-1} are remarkably low values compared to other materials under consideration.

With these results we can calculate the thermal conductivity $\lambda(T)$ according to $\lambda(T) = \rho(T)c(T)\mu(T)$ taking into account the temperature dependence of the mass

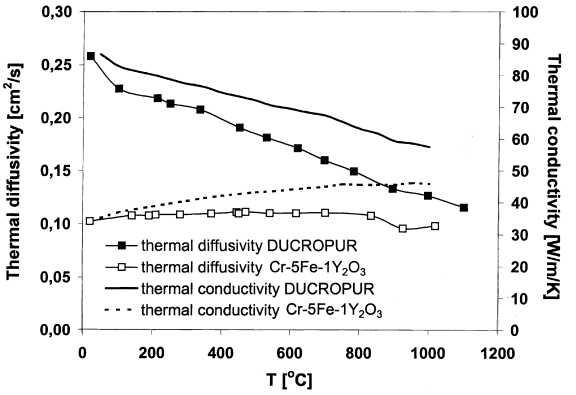

Fig. 1. Thermal diffusivity $\mu(T)$ of DUCROPUR and Cr·5Fe·$1Y_2O_3$ measured by the laser flash method and the thermal conductivity $\lambda(T)$ calculated from $\mu(T)$, the heat capacity $c(T)$ and the thermal expansion $\alpha_m(T)$.

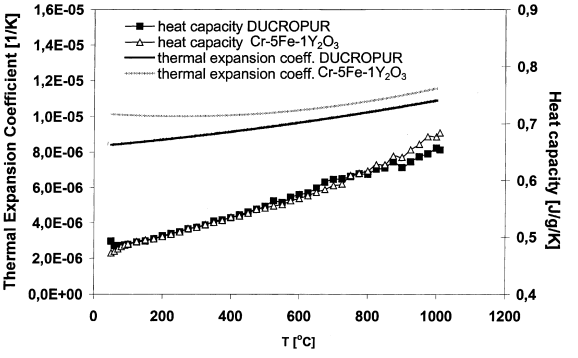

Fig. 2. Temperature dependence of the heat capacity $c(T)$ at constant pressure and of the average thermal expansion coefficient α_m of DUCROPUR and Cr·5Fe·$1Y_2O_3$.

density $\rho(T) = \rho_0(1 - 3\alpha_m T)$. The calculated values are included in Fig. 1.

3.2. Mechanical tests

The tensile properties of the investigated materials i.e., the yield stress σ_y and the ultimate tensile strength σ_{UTS} are shown in Fig. 3. The strain rate calculated from the constant cross-head speed was about 10^{-3} s^{-1}. As in many body centred cubic metals, yield point phenomena were observed at lower temperatures. In these cases σ_y-values refer to the lower yield stress while σ_y denotes the flow stress at 0.2% elongation in the absence of yield phenomena. In Fig. 3, tensile data from $Cr \cdot 5Fe \cdot 1Y_2O_3$ sheet material [9] with a thickness of 2.5 and 5 mm (pre-deformation of 94% and 88%, respectively) are included. The data presented here agree quite well with the 2.5-mm thick and 94% pre-deformed material.

In all cases, difficulties occurred at lower test temperatures due to the brittleness of the materials and the resulting sensitivity to surface imperfections, which caused premature failure.

In [10], tensile tests at strain rates ranging from 5×10^{-5} to 8.5×10^{-4} s^{-1} were performed on DUCROPUR, but no significant influence on the tensile properties was observed. Fig. 3(a) and (b) include data obtained from cylindrical specimens with a diameter of 4 mm, which exhibit a slightly lower yield stress. The ultimate tensile strength σ_{UTS} depends on the specimen geometry.

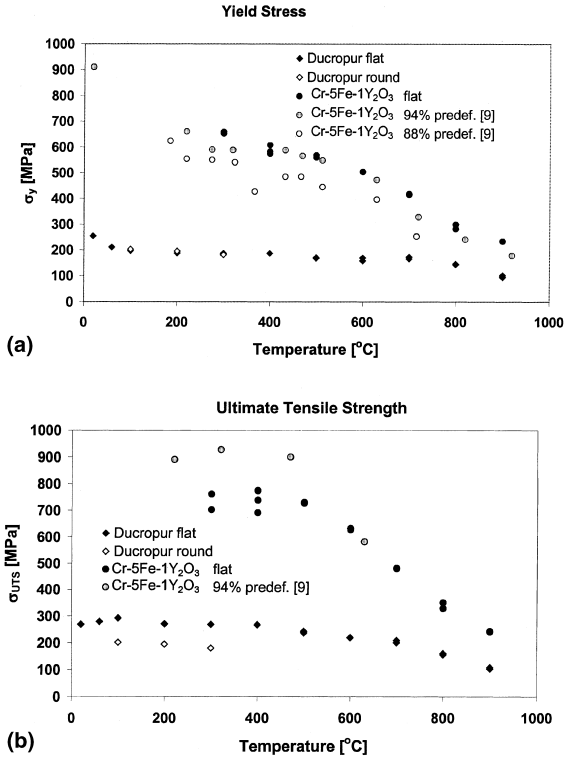

Fig. 3. Tensile properties of DUCROPUR, $Cr{\cdot}5Fe{\cdot}1Y_2O_3$ and as a function of temperature: (a) yield stress; (b) ultimate tensile stress.

The elongation at fracture [2] indicates a brittle behaviour of the $Cr \cdot 5Fe \cdot 1Y_2O_3$ alloy, which shows some ductility at rupture only at temperatures above 200°C. DUCROPUR shows a more ductile behaviour; however, cleavage rupture is still observed in the fracture tests even at temperatures where the elongation at rupture is greater than 10% [2].

3.3. Refinement of microstructure

Transmission electron microscopy, selected area electron diffraction patterns and X-ray texture measurements revealed that severe torsional deformation introduced an ultra-fine grained structure with high-angle grain boundaries. The dislocation density in these grain boundaries was determined to be up to 1×10^{15} m^{-2} whereas it was about three orders of magnitude lower in the cell interior. At a deformation temperature of 540°C a mean grain size of 0.3 μm in DUCROPUR and of 0.5 μm in $Cr \cdot 5Fe \cdot 1Y_2O_3$ was obtained, equivalent to a refinement by a factor of about 260 and 22, respectively. The different degree of obtainable refinement may be due to the different initial grain size, but may also be affected by the Y_2O_3 particles.

In the case of DUCROPUR the microstructure refinement was accompanied by an increase of the Vickers microhardness from 1.75 GPa to above 6 GPa and to about 3 GPa for processing at room temperature and at 540°C, respectively. Annealing for 30 min showed that the ultra-fine microstructure was stable up to about 450°C. Annealing at 900°C re-established the initial hardness value before processing.

Tensile tests in the temperature range between 20°C and 350°C were performed on DUCROPUR after microstructure refinement. They showed that for example at 300°C an ultimate tensile strength of 480 MPa was obtained, which is twice as high as in the coarse grained material. In Fig. 4, the stress displacement curves for bending tests at 100°C are shown, which indicate that severe plastic torsional deformation at 540°C yields an appreciable strengthening of the material without an apparent loss of ductility. Moreover, taking the difference between σ_{UTS} and the rupture stress σ_r as indicator for ductility, a considerable improvement is achieved from 107 to 476 MPa for coarse (initial) and fine-grained (processed) material, respectively. Similar values were obtained for bending at 200°C whereas at room temperature no effect was visible.

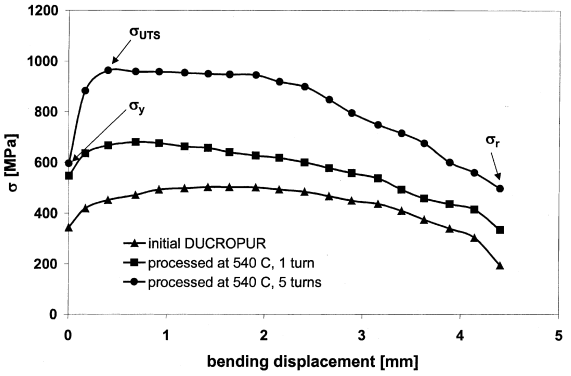

Fig. 4. Stress–bending displacement curves for DUCROPUR before and after processing by severe plastic torsional deformation measured at 100°C.

4. Discussion and conclusions

The thermo-mechanical properties were measured in the temperature range between 20°C and 900°C in view of higher operation temperatures of future fusion reactors where Cr alloys will show their full advantages. Properties at lower temperatures are important for materials processing and relevant for the start-up and shutdown procedures.

The lower thermal conductivity of $Cr \cdot 5Fe \cdot 1Y_2O_3$ compared with pure chromium in Fig. 1 can be understood by the solid solution of Fe in the chromium matrix which reduces the lattice symmetry and increases the number of scatter centres for phonons and electrons, thus reducing the thermal conductivity. Neither an effect of grain size, nor of the dispersed Y_2O_3 particles can be expected. The solid solution of Fe in Cr also changes the interatomic potential, for which the asymmetry gives rise to the thermal expansion. Thus, the alloying effect observed in Fig. 2 is plausible.

The preliminary results of the mechanical properties after microstructural refinement by severe plastic deformation indicate that this method may be a starting point for improving the low temperature mechanical properties of DUCROPUR and $Cr \cdot 5Fe \cdot 1Y_2O_3$. For higher service temperatures, however, methods have to be developed to stabilize the refined microstructure. An analysis in terms of the Hall–Petch relation $\sigma_y = \sigma_0 + Kd^{-1/2}$, where K is a constant and d denotes the subgrain size, shows that the increase of σ_y is lower than expected from the reduction in grain size. Hence, one has to conclude that the threshold stress σ_0 is appreciably modified by microstructure refinement.

First wall and blanket components are subject to cyclic thermal loading. The thermal stress factor defined as $\alpha E/[\lambda(1-\nu)]$ (E is Young's modulus, α the thermal expansion coefficient, λ the thermal conductivity and ν is the Poisson's ratio) gives an estimate of the magnitude of thermal stresses during thermal transients. For DUCROPUR, a very low value compared to other low activation materials is obtained (at 20°C, about 0.031 MPa m/W) due to the favourable combination of a high thermal conductivity and a low thermal expansion coefficient. This may compensate for the low temperature brittleness by maintaining low thermal stress levels under a given heat flux load.

From the two materials discussed here, $Cr \cdot 5Fe \cdot 1Y_2O_3$ combines excellent low activation characteristics with a relatively high strength. Low fracture toughness values and the propensity to brittle fracture up to 500°C may limit its possible use [2], if the gain in ductility achieved by severe plastic deformation cannot be obtained in components. DUCROPUR has a significantly lower strength but its fracture toughness values are significantly higher than in $Cr \cdot 5Fe \cdot 1Y_2O_3$ indicating a ductile to brittle transition temperature of about 300°C [2]. Ductility will be further improved choosing high purity grades of Cr with even better low activation characteristics.

The irradiation-induced degradation of the mechanical properties of high-purity chromium and $Cr \cdot 5Fe \cdot 1Y_2O_3$ has not yet been explored. Investigations on Fe–Cr alloys with chromium contents in the range between 9 and 50 wt% indicate embrittlement due to the irradiation-induced formation of dislocation loops and α'-phase at these loops [11,12]. Although the α'-phase is formed more easily in the chromium-rich alloys the growth of the loops is slower there [5]. The irradiation-induced formation of the brittle σ-phase [13] may effectively be minimized in the case of $Cr \cdot 5Fe \cdot 1Y_2O_3$ and will not be an issue for pure chromium. Thus, an improvement in the radiation resistance over the already tested chromium alloys might be expected.

References

[1] M. Zucchetti, M. Merola, J. Nucl. Mater. 233–237 (1996) 1486.
[2] H. Stamm, M.R. Bonansinga, F. Dos Santos Marques, P. Hähner, H. Kolbe, A. Volcan, J. Nucl. Mater. 258–263 (1998) 1756.
[3] W.D. Klopp, J. Met. (Nov. 1969) 23.
[4] W.D. Klopp, J. Less Common Met. 42 (1975) 261.
[5] A. Hishinuma, S. Isozaki, S. Takaki, K. Abiko, Phys. Stat. Sol. A 160 (1997) 431.
[6] I.V. Alexandrov, Y.T. Zhu, T.C. Lowe, R.K. Islamgaliev, R.Z. Valiev, NanoStructured Mater. 10 (1998) 45.
[7] R.Z. Valiev, Ann. Chim. 21 (1996) 369.
[8] J. Parker, R.J. Jenkins, C.P. Butler, G.L. Abbot, J. Appl. Phys. 32 (1961) 1679.
[9] M. Janousek, Fortschr.-Ber. VDI Reihe 5 Nr. 476, VDI Verlag, Düsseldorf, 1997.

[10] J. Heieck, EUR 17290 EN, 1997.
[11] E. Wakai, A. Hishinuma, Y. Kato, H. Yano, S. Takaki, K. Abiko, J. Phys. Coll. C7 (Suppl. III) 5 (1995) 277–286.
[12] E. Wakai, A. Hishinuma, T. Sawai, S. Kato, S. Isozaki, S. Takaki, K. Abiko, Phys. Stat. Sol. A 160 (1997) 441.
[13] V. Chakin, V. Kazakov, Yu. Goncharenko, Z. Ostrovsky, J. Nucl. Mater. 233–237 (1996) 573.