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Thermomechanical characteristics of low activation chromium and chromium alloys

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Abstract

The paper presents results of measurements concerning basic thermomechanical properties of sintered high purity chromium and two sintered Cr–Fe alloys, i.e. Cr 5Fe $1Y_2O_3$ and Cr 44Fe 5Al 0.3Ti $0.5Y_2O_3$ investigated in the temperature range from room temperature to 600°C. The materials were characterized by tensile testing, measurements of thermal diffusivity, metallographic characterization and fractographic studies. The results are discussed with regard to transient thermal loading faced by first wall structures. In order to address the critical issue of brittleness, fracture mechanics tests have been performed which give indications on the ductile to brittle transition temperature. Results for the temperature dependence of the fracture toughness of high purity chromium are presented. Fracture mechanisms in the above mentioned temperature range are discussed on the basis of microstructural analyses by optical and scanning electron microscopy.

1. Introduction

The low activation properties of chromium have created interest in studies of Cr and Cr alloys in the fusion long-term programme in order to explore their potential as structural material in fusion reactors for example as first wall or blanket materials. Recent investigations [1,2] have shown that the two commercially available materials high purity chromium (DUCROPUR™ [1]), and the alloy Cr 5Fe $1Y_2O_3$ show excellent low activation characteristics. In particular, a first wall made of DUCROPUR may be classified as 'Low Level Waste' after 50 years of cooling [2]. Neither SiC/SiC composites nor V–5Ti fall into this classification. The activation characteristics of the alloy Cr 44Fe 5Al 0.3Ti $0.5Y_2O_3$ are less favourable, however, the material can still be classified as 'Medium Level Waste' after 50 years of cooling.

Chromium and chromium alloys have been studied in the 50 and 60 s in order to explore possible high temperature applications in jet engines in competition with nickel based superalloys [3,4]. Chromium alloys exhibit a favourable strength to density ratio combined with a rather high elastic modulus and a high melting point. Serious drawbacks, the most important ones being the embrittlement from nitrogen contamination at elevated temperatures and the unacceptably high ductile to brittle transition temperature of high strength chromium caused the loss of interest in these alloys and gave preference to superalloys.

Material requirements of fusion reactors, especially with regard to the low activation aspect and favourable properties to withstand severe cyclic thermal loading, have again drawn the attention to chromium alloys. Due to the high thermal conductivity going along with a low thermal expansion coefficient, much lower thermal stresses under transient thermal loading are induced as compared to steels and other materials. In this paper the thermomechanical properties of the above mentioned Cr based materials are discussed and compared with those of other low activation materials (LAM). New fracture toughness measurements are reported which show that the risk of brittle failure persists up to about 500°C.

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2. Materials and test methods

Material: The materials investigated were 99.7% pure chromium (DUCROPUR™) and the Cr–Fe alloys Cr 5Fe 1Y_2O_3 and Cr 44Fe 5Al 0.3Ti 0.5Y_2O_3 which were commercially available from the Metallwerke Plansee AG, Austria. All these materials were produced in a special sintering process. The chemical composition analyses as given by the manufacturer are compiled in Table 1. The material was available in the form of plates of the dimension 350 mm × 305 mm × 15 mm (length × width × thickness).

Thermal diffusivity: The laser flash method [5,6] has been used for the determination of the thermal diffusivity in the range from room temperature up to 600°C. The measurements were performed using small specimens of 1.5 mm thickness which 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.

Tensile testing: Displacement controlled tests under constant crosshead speed were performed in air in the temperature range from room temperature to 400°C using electro-mechanical testing machines. Different types of specimens (flat and cylindrical) were tested with different crosshead speeds. The flat specimens had cross-sections of 4 mm × 1 mm and the round specimens a diameter of 4 mm in the gauge length.

Fracture mechanics testing: The fracture mechanics tests were performed in air in the temperature range from room temperature to 500°C with an MTS servo-hydraulic testing machine (MTS, series 810). Compact tension test specimens according to ASTM-E399-90 with thickness $B = 15$ mm were cut by spark erosion from DUCROPUR and Cr 5Fe 1Y_2O_3 plates. Chevron notches were introduced to facilitate the initiation of a crack that was propagated by fatigue to the required length. At low temperatures (i.e. less than 200°C), this was not possible due to the high brittleness of the material causing unstable cleavage fracture from the Chevron notch or before the fatigue crack was sufficiently long. The fracture toughness results obtained in terms of critical stress intensity factors K_Q were not valid K_{Ic}-values according to the ASTM standard. At temperatures below 200°C the K_Q values are calculated from the maximum load and the fatigue crack length observed after rupture. These values can be considered as an upper bound of the fracture toughness.

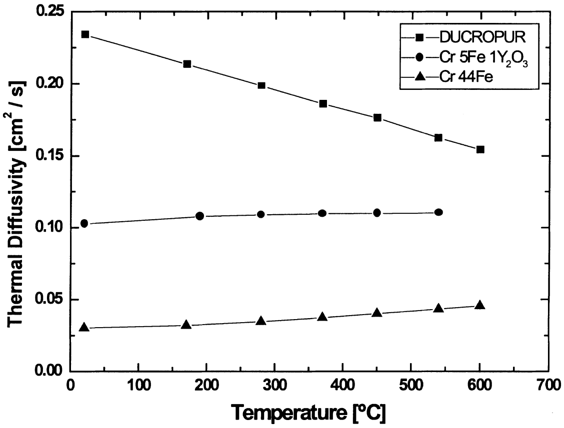

Fig. 1. Thermal diffusivity of DUCROPUR, Cr 5Fe 1Y_2O_3 and Cr 44Fe 5Al 0.3Ti 0.5Y_2O_3.

3. Results

3.1. Thermal properties

The thermal diffusivity of chromium and the two Cr-alloys was measured by using the laser flash method and is illustrated in Fig. 1. It can be seen that the unalloyed Cr has a high thermal diffusivity μ from which the thermal conductivity λ can be calculated according to $\lambda = \rho c \mu$ where c is the specific heat and ρ the mass density. The thermal diffusivities of the Cr–Fe-alloys are significantly lower than that of DUCROPUR and show little temperature dependence.

Table 1
Chemical composition of the investigated materials (guaranteed analysis for DUCROPUR and typical analyses for Cr-alloys)

Element	DUCROPUR Cr 99.7%	Cr 5Fe 1Y_2O_3	Cr 44Fe 5Al 0.3Ti 0.5Y_2O_3
O	<0.01 wt%	0.43%	0.31%
N	<0.005 wt%	115 ppm	270 ppm
H	<0.0005 wt%	5 ppm	5 ppm
C	<0.01 wt%	15 ppm	98 ppm
Fe	<0.25 wt%	5.3%	43.6%
Y	–	0.68%	0.37%
Al	<0.001 wt%	–	4.77%
Ti	–	–	0.21%
Mo	<0.0002 wt%	<0.0002 wt%	<0.0002 wt%

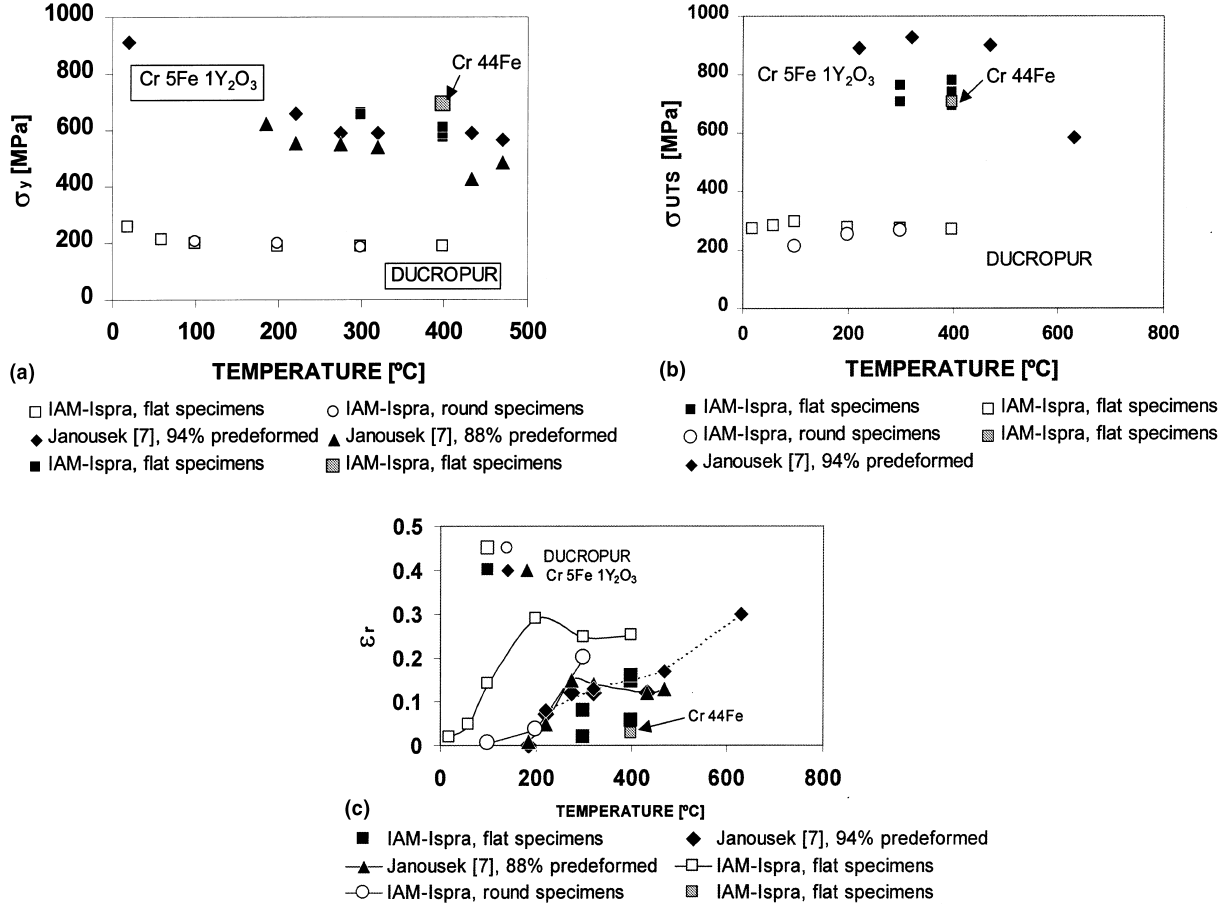

Fig. 2. Tensile properties of DUCROPUR, Cr 5Fe 1Y_2O_3 and Cr 44Fe 5Al 0.3Ti 0.5Y_2O_3 as a function of temperature. (a) Yield stress. (b) Ultimate tensile stress. (c) Elongation at rupture.

DUCROPUR has a remarkably low linear thermal expansion coefficient α_m. The mean coefficient between room temperature and 100°C is $\alpha_m = 6.9 \times 10^{-6}$ K^{-1} and $\alpha_m = 8.6 \times 10^{-6}$ K^{-1} in the range up to 500°C as given by the manufacturer. A similar value is known for the alloy Cr 5Fe $1Y_2O_3$ with $\alpha_m = 8.9 \times 10^{-6}$ K^{-1} between room temperature and 500°C [7].

3.2. Tensile tests

The tensile properties of the investigated materials i.e. the yield stress σ_y, the ultimate tensile strength σ_{UTS}, and the elongation at rupture ε_r are presented in Fig. 2. For the tests presented here the strain rate calculated from the constant crosshead speed was about 10^{-3} s^{-1}. As is typical for many polycrystalline b.c.c. 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. 2, tensile data from Cr 5Fe $1Y_2O_3$ sheet material with a thickness of 2.5 mm and 5 mm, (pre-deformation of 94% and 88%, respectively) [7] are included. The data presented here agree quite well with the 2.5 mm (94% pre-deformed) material.

In all cases, difficulties occurred in tests at lower temperatures due to the brittleness of the materials and the resulting sensitivity to surface imperfections. This caused premature failure in the elastic range or at the pinholes. In the case of Cr 44Fe 5Al 0.3Ti $0.5Y_2O_3$, an inelastic range was observed only in the 400°C test.

In Ref. [8], tensile tests at different constant crosshead speeds were performed for DUCROPUR resulting in strain rates from 5×10^{-5} to 8.5×10^{-4} s^{-1}, however, no significant influence of strain rate on the tensile properties was found. Fig. 2(a) and (b) include data obtained from cylindrical specimens with a diameter of 4 mm which coincide with the yield stress of the flat specimens. The ultimate tensile strength σ_{UTS} shows only a slight dependence on specimen geometry.

The elongation at fracture (Fig. 2(c)) reflects the quite brittle behaviour of the Cr–Fe alloys which show some ductility at rupture only at temperatures above 200°C. DUCROPUR shows a more ductile behaviour with a significant difference between the flat and the cylindrical specimens. It is worthwhile mentioning that at temperatures where the elongation at rupture is greater than 10%, cleavage rupture is still observed in the fracture mechanics tests.

3.3. Fracture mechanics tests

Fracture mechanics tests for the determination of fracture toughness in terms of K_{Ic} or J_{Ic} were performed for DUCROPUR and Cr 5Fe $1Y_2O_3$. The results are plotted in Fig. 3. In terms of the ASTM E399-90 standard no valid K_{Ic}-value (and therefore denoted as K_Q in Fig. 3) were obtained in DUCROPUR. The circular symbols represent measurements where unstable failure initiated at a fatigue pre-crack that fulfilled the length requirements of the standard. The non-validity with regard to the standard was due to violation of the size requirements (for values in DUCROPUR above 15.5 MPa$\sqrt{m}$) and partially due to the testing procedure. At the higher temperatures, a J_{Ic} test according to the

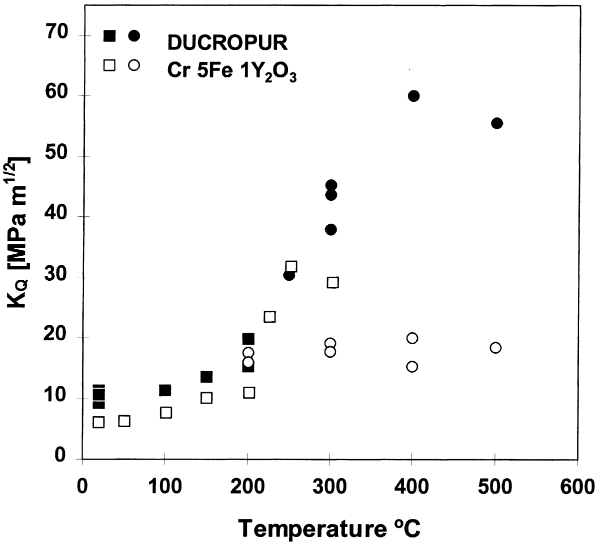

Fig. 3. Fracture toughness of DUCROPUR (filled symbols) and Cr 5Fe $1Y_2O_3$ (open symbols) as a function of temperature. The filled squares indicate estimations from uncracked specimens, the open and filled circles give results where cleavage rupture initiated in a pre-cracked specimen. The open squares refer to data from [7].

compliance test method was performed to determine the amount of ductile crack growth prior to cleavage failure. The K_Q results evaluated from the initiation of cleavage fracture may be influenced by the pre-deformation of the crack tip region before cleavage fracture intervened.

The filled squares represent measurements in DUCROPUR where cleavage fracture occurred before a sufficiently long fatigue crack had grown. The values must be considered as upper bounds for the fracture toughness in this temperature range.

The results for DUCROPUR show an upswing of toughness at about 200°C thus indicating a ductile to brittle transition. However, even at test temperatures of 500°C cleavage fracture was observed after a small amount of ductile crack growth. Further tests are necessary in order to determine the temperature where the material fails completely by ductile tearing without mode conversion to cleavage.

The fracture toughness results obtained in Cr 5Fe $1Y_2O_3$ with CT specimens are represented by the open circles. In addition, data from [7] are included which have been obtained from notched 4-point bending specimens with 5 mm thickness. Due to size requirements, valid K_{Ic} values are limited to about 25 MPa$\sqrt{m}$. Taking into account that no pre-crack was introduced, these data should be considered as upper bounds, too. Our measurements are in good agreement at 200°C but indicate rather low K_Q values of about 15–20 MPa$\sqrt{m}$ up to a temperature of 500°C where cleavage fracture is still observed.

3.4. Microstructural investigations

The microstructural investigations were performed by optical and scanning electron microscopy (SEM). The grain size was determined after electrolytic etching using the lineal intercept method. The grain size was 82 μm in DUCROPUR, 11 μm in Cr 5Fe $1Y_2O_3$ and 200 μm in Cr 44Fe 5Al 0.3Ti $0.5Y_2O_3$.

SEM was used for fractographic studies of tensile specimens and CT specimens. The fracture surfaces were examined with regard to fracture mode and crack initiation sites. In the cylindrical tensile specimens, no significant reduction of the cross-section was observed up to 300°C in contrast to the flat specimens where at 300°C some and at 400°C considerable necking occurred. In general, the fracture surfaces are oriented perpendicular to the loading direction. Tear ridges separate transgranular cleavage planes with the characteristic river patterns. Cleavage fracture initiation points, frequently close to the border, were found in most of the specimens and could be associated with discontinuities such as inclusion particles. In Cr 5Fe $1Y_2O_3$, again transgranular brittle fracture, characterized by typical cleavage planes, occurs. Fracture initiation points are close to the borders and are associated with stringers. At 400°C mixed transgranular and intergranular fracture is found.

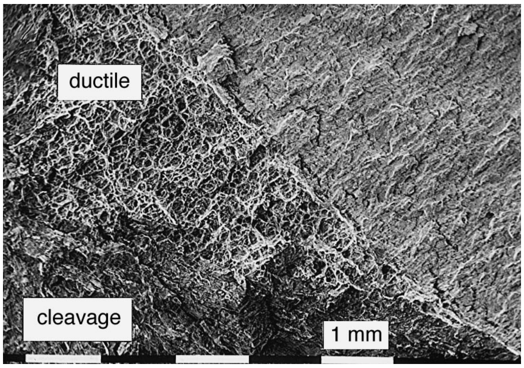

Fig. 4. Fracture surface of a DUCROPUR CT-specimen broken at 400°C. A small zone of ductile crack growth can be distinguished from the pre-crack and the cleavage rupture.

In Fig. 4, the fracture surface of a DUCROPUR CT-specimen broken at 400°C is shown. The fatigue pre-crack is well distinguishable from a zone in the centre of the specimen with ductile crack growth and from the subsequent cleavage zone. Such zones with ductile crack growth prior to cleavage failure were only observed in specimens tested at temperatures ⩾ 250°C. At 300°C, ductile zones with a width of about 2 mm in the centre of the specimen were found. At the lateral specimen surface, where plastic deformation and some necking occurs, the zone width is much smaller and sometimes hardly visible.

Fractographic studies of the Cr 5Fe $1Y_2O_3$ CT-specimens did not show a ductile crack growth zone in the whole temperature range investigated. Cleavage fracture occurs in all cases without visible plastic deformation at the lateral specimen surfaces.

4. Discussion and conclusions

The thermo-mechanical results presented here were measured in the temperature range between 20°C and 500°C that covers the range of the design temperature for actual experimental fusion reactors under development. Future reactors may operate at higher temperatures where the material properties of Cr will show to advantage. Properties at lower temperatures are important characteristics for materials processing and workability and are relevant for the start-up and shutdown procedures.

First wall and blanket components are subject to cyclic thermal loading. The thermal stress factor defined as $\alpha E/[\lambda(1-\nu)]$ (E: Young's modulus, α: thermal expansion coefficient, ν: Poisson's ratio) gives an estimate of the magnitude of thermal stresses in materials exposed to thermal transients. For DUCROPUR, e.g., a very low value compared to other low activation materials results (at 20°C about 0.034 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 three materials discussed here, Cr 44Fe 5Al 0.3Ti 0.5Y_2O_3 seems to be less suited due to its extremely low ductility and less favourable low activation properties [1,2]. Cr 5Fe 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. DUCROPUR has a significantly lower strength but displays a higher ductility as found in tensile tests. Fracture toughness values are significantly higher than in Cr 5Fe 1Y_2O_3 indicating a ductile to brittle transition temperature of about 300°C. Ductility will be further improved choosing high purity grades of Cr with even better low activation characteristics.

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References

[1] M. Zucchetti, M. Merola, J. Nucl. Mater. 233–237 (1996) 1486.

[2] M. Zucchetti, private communication, 1997.

[3] W.D. Klopp, J. Metals, November (1969) 23.

[4] W.D. Klopp, J. Less Common Met. 42 (1975) 261.

[5] J. Parker, R.J. Jenkins, C.P. Butler, G.L. Abbot, J. Appl. Phys. 32 (1961) 1679.

[6] M. Oksanen, A. Volcan, P. Fenici, L. Fabbri, to be published.

[7] M. Janousek, Fortschr.-Ber. VDI Reihe 5 Nr. 476, VDI Verlag, Düsseldorf, 1997.

[8] J. Heieck, EUR 17290 EN, 1997.