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Thermal fatigue testing of CuCrZr alloy for high temperature tooling applications

Yucel Birol

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Abstract CuCrZr alloy offers good mechanical and thermal properties and was investigated in the present work for its potential as tooling material in thixoforming of steels. Samples of CuCrZr alloy were cycled thermally between 450 and 750 °C, every 60 s. The thermal conductivity of the CuCrZr alloy, nearly an order of magnitude higher with respect to that of the conventional hot work tool steel, proved to be very beneficial in terms of thermal stresses generated at the surface upon thermal cycling. The maximum compressive and tensile stresses produced at the front face of the CuCrZr alloy were estimated to be approximately 30 and 10 MPa, respectively, much smaller than those endured by the conventional hot work tool steel. The very favourable thermal stress state in the CuCrZr alloy die was largely negated, however, due to its inferior resistance to high temperature oxidation.

Introduction

Cyclic thermal loading on tools is substantial when steel parts are to be formed in the semi-solid state. This imposes several requirements on tool materials, which cannot be fulfilled by hot work tool steels [1–10]. Potential alternatives include hard metals and bulk ceramics [11–14]. The titanium–zirconium–molybdenum based high temperature alloy (TZM) has shown encouraging results [3] but suffers extensive oxidation [15]. Silicon nitride (Si_3N_4)-based materials show exceptional fracture toughness and thermal shock resistance as well as high strength but are sensitive to oxidation and corrosive attack above 1,100 °C [16]. Ni-, Co- and Cr-based high temperature alloys were shown to perform better than hot work tool steels under steel thixoforming conditions owing to a superior high temperature oxidation resistance [17–24].

Alternatively, die materials with a high thermal conductivity also deserve attention. Copper-based dilute alloys are commonly used in heat transfer elements, because of their excellent thermal conductivity, strength, and fatigue resistance [25]. The main attraction of copper-based alloys lies in their high thermal conductivity, which is at least 10 times greater than that of most steels. This high conductivity assists heat removal and thereby reduces the thermal stresses, which lead to thermal fatigue. Hence, thermal fatigue cracking is not a typical failure mode in resistance welding electrodes manufactured from high conductivity copper alloys. Of the several dilute Cu-based alloys, CuCrZr alloy offers good mechanical and thermal properties [26] and was investigated in the present work for its potential as tooling material in thixoforming of steels.

Experimental

The thermal fatigue tests involved cyclic heating and cooling of prismatic bars (25 mm × 25 mm × 20 mm) machined from CuCrZr alloy (Table 1) between the peak die cavity surface temperature and the temperature the die was pre-heated to before the forming operation [22]. The former was measured during thixoforming experiments with slugs sectioned from a commercial hot rolled X210CrW12 bar. These slugs were heated to 1,290 °C before forming into dies manufactured from CuCrZr alloy, with a cylindrical cavity (60 mm, ∅50 mm). A K-type thermocouple was fixed in a 3-mm diameter hole, drilled

Y. Birol (✉)
Materials Institute, Marmara Research Center, TUBITAK, Gebze, Kocaeli, Turkey
e-mail: yucel.birol@mam.gov.tr

Table 1 Chemical composition of the CuCrZr alloy used in the present work (wt%)

Cu	Cr	Zr	Fe[a]	Zn[a]	Si[a]	Sn[a]	Pb[a]
98.78	0.63	0.55	185	62	31	11	11

[a] ppm

horizontally at 20 mm from the die entry and 0.1 mm from the die cavity surface. The temperature of the die cavity surface was recorded with an *X–Y* recorder once the slurry was forced into the die.

The front face of the sample was heated by an oxyasetilen flame to the maximum die cavity surface temperature thus measured within about 30 s, while cooling was performed by forced air to 450 °C, the die pre-heat temperature, during the next 30 s (Fig. 1). This provided a 1-min long thermal cycle, which approximated the industrial steel thixoforming cycle. The temperatures at the front and rear faces of the samples were measured during thermal cycling with K-type thermocouples fixed into 3-mm diameter holes 0.1 mm from respective surfaces. The stress state produced by thermal cycling at the front face of the sample is schematically illustrated in Fig. 1c. Thermal fatigue damage was assessed qualitatively using stereo and light microscopy.

The hardness of the samples was measured in Vickers units with a load of 1 kg (HV1) before and during thermal cycling. The thermal expansion coefficients of the potential die materials were determined with a Netzsch 402 PC unit in air at a scanning rate of 10 K min^{-1}. A Netzsch LFA457 instrument was used for thermal conductivity measurements under nitrogen gas flowing at 100 mL min^{-1}, at a heating rate of 5 K min^{-1}.

Thermo gravimetric analysis (TGA) was performed with a SETARAM TG/DTA unit to determine the oxidation behaviour of the CuCrZr alloy. Powder sample pulverized via mechanical means, with an average grain size of 45 µm, were placed in deep platinum pans and were heated in flowing oxygen at 10 °C min^{-1} until 800 °C. A Shimadzu XRD-6000 model X-ray diffractometer equipped with Cu*Kα* radiation was employed for the identification of oxides on the surfaces of the samples submitted to annealing at 800 °C.

Results and discussion

Thermophysical properties of the die materials have a big impact on temperature gradients, which in turn, dictate the magnitude of thermal stresses across the die. High thermal conductivity promotes the extraction of heat from the die, avoids high surface temperatures and thereby works against steep thermal gradients while low thermal expansion coefficients reduce thermal stresses [6]. However, for thermal expansion behaviour to impact thermal stress state,

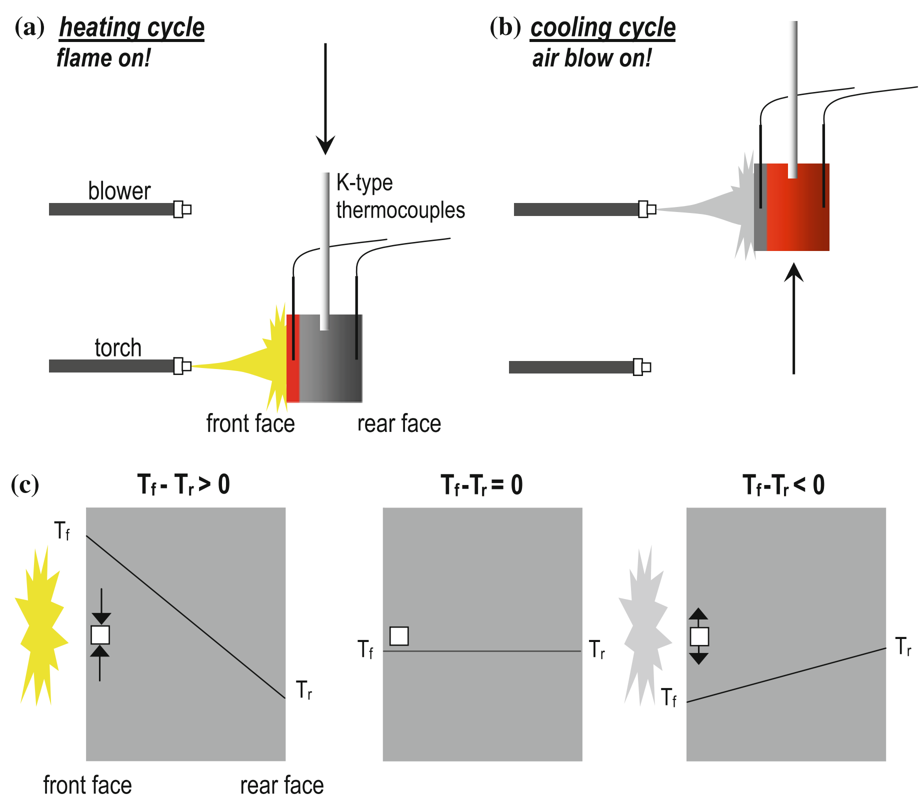

Fig. 1 Schematic illustration of the thermal fatigue test: **a** heating and **b** cooling cycle, and of **c** the thermal stress states produced during thermal cycling

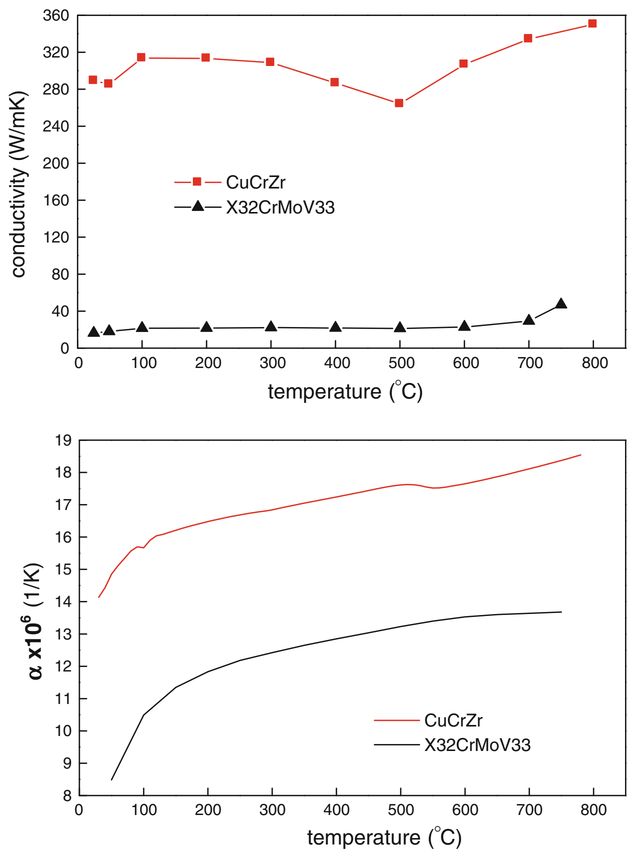

Fig. 2 Change in thermophysical properties with temperature of the CuCrZr alloy and the X32CrMoV33 hot work tool steel

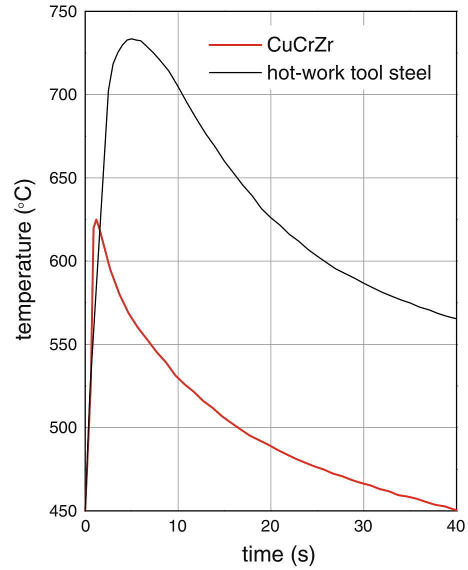

Fig. 3 Change in die cavity surface temperature with time of the CuCrZr alloy and the X32CrMoV33 hot work tool steel during thixoforming steels

thermal gradients must develop across the die first. Hence, thermal conductivity is the more critical of these thermophysical properties. CuCrZr alloy enjoys a very high thermal conductivity, but is inferior with respect to the conventional hot work tool steel, X32CrMoV33, in terms of thermal expansion behaviour (Fig. 2).

The very high thermal conductivity of the CuCrZr alloy is reflected not only by the change in die cavity surface temperature upon thixoforming but also by the thermal cycles recorded during thermal fatigue tests. The maximum die cavity surface temperature attained upon steel thixoforming was measured to be approximately 620 °C, relatively smaller with respect to a conventional hot work tool steel die (Fig. 3). Despite fixed maximum and minimum front face temperatures and fixed heating/cooling steps of 30 s employed in thermal fatigue tests, thermal cycling generates T versus t curves in the CuCrZr alloy samples markedly different from those in a hot work tool steel as well as in Cr-, Ni- and Co-based superalloys [17, 22]. Front and rear face temperatures run very close to each other throughout the entire thermal cycle and thus imply a uniform temperature distribution across the section of the CuCrZr alloy sample owing to the perfect conduction of heat supplied at the front face (Fig. 4a). This is in marked contrast to the hot work tool steel die sample, which enjoys such a homogeneity very briefly only twice during the entire cycle when the front and rear face temperatures were in close proximity (Fig. 4b).

The thermal cycles at the opposite faces of the CuCrZr alloy sample are nearly identical producing a much smaller temperature gap (Fig. 5a). The rear face of the X32CrMoV33 hot work tool steel sample, on the other hand, was cycled between 565 and 480 °C, while the front face goes through the intended peak temperatures every 30 s. This relatively smaller amplitude, together with the displacement of the thermal cycle, due to an apparent delay in both heating and cooling of the rear face, produces a temperature gap across the section of the X32CrMoV33 sample, which becomes as large as 200 °C, 20 s into the cycle (Fig. 5a).

Having established the change in temperature gap with time during a typical thermal cycle, ΔT versus t, the thermal stresses generated at the front face, i.e. the die cavity surface, during thermal cycling can be estimated from, $\sigma_{surface} \cong \alpha(T) \cdot E(T) \cdot (\Delta T)$ [27]. α and E are the thermal expansion coefficient and the Young's modulus, respectively, both expressed as a function of temperature. The evolution of thermal stresses during a typical thermal cycle thus obtained is shown in Fig. 5b. Thermal cycling produces compressive stresses at the front face when it is warmer than the bulk, i.e. when the mushy feedstock is forced into the die during thixoforming operation. The maximum compressive stress acting on the front face is estimated to be approximately 30 MPa and dominates for

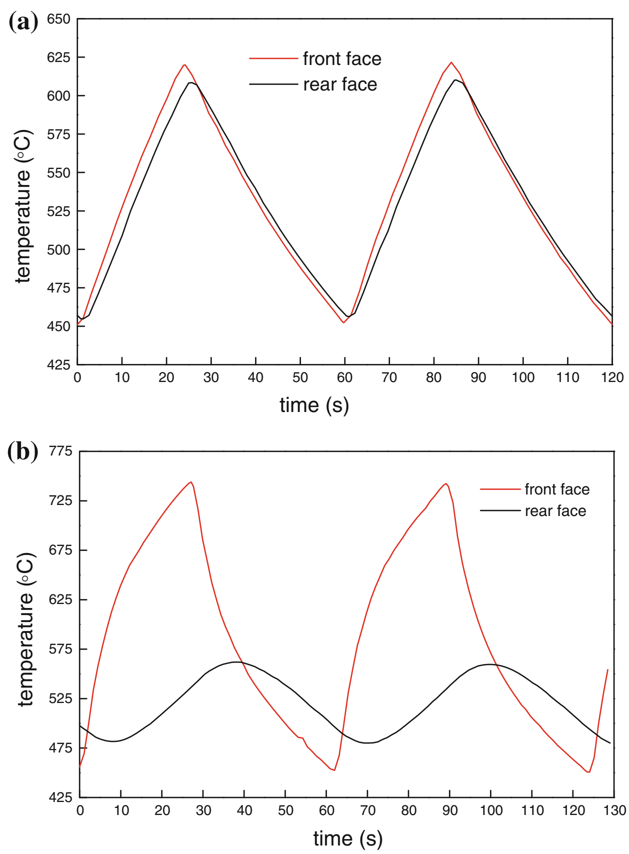

Fig. 4 Change in temperature with time at the front and rear faces of **a** the CuCrZr alloy and **b** the X32CrMoV33 hot work tool steel samples during thermal cycling

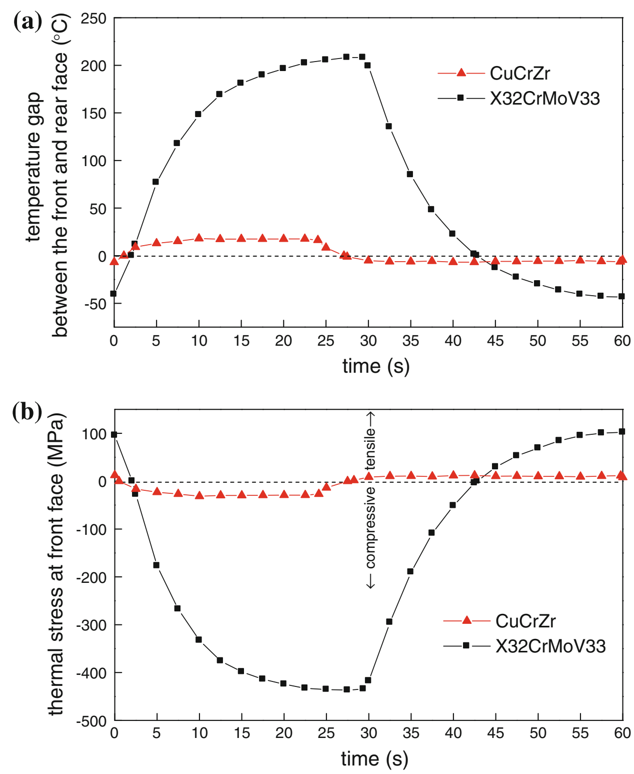

Fig. 5 Change in **a** the temperature gap between the front and rear faces and in **b** the thermal stresses generated at the front face with time during thermal cycling of the CuCrZr alloy and the X32CrMoV33 hot work tool steel samples

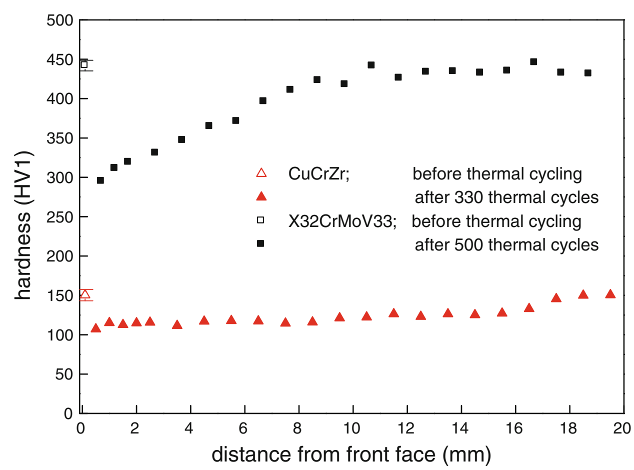

Fig. 6 Change in hardness with depth from the front face before and after thermal cycling of the CuCrZr alloy and the X32CrMoV33 hot work tool steel samples

nearly the entire heating step. Tensile stresses take over when the front face cools below the bulk. This occurs when the forming operation is over and the thixoformed part is ejected from the die. The maximum tensile stress generated at the front face during the cooling step is approximately 10 MPa. The maximum compressive and tensile stresses that develop at the front face during thermal cycling of the CuCrZr alloy sample are safely below the fatigue endurance limit reported for the CuCrZr alloys [28] and are much smaller than those for the X32CrMoV33 sample, estimated to be approximately 400 and 100 MPa, respectively (Fig. 5b). It is thus fair to conclude that the thermal conductivity of the CuCrZr alloy, nearly an order of magnitude higher with respect to those of X32CrMoV33, more than compensates for its higher thermal expansion coefficient. CuCrZr alloy thus appears to be the better tooling material in terms of thermophysical properties, which help to reduce the magnitude of thermal stresses acting on the die cavity surface.

While the CuCrZr alloy offers exceptional thermal fatigue resistance, it suffers a substantial drop in hardness upon thermal cycling under steel thixoforming conditions (Fig. 6). The average hardness of the thermal fatigue sample, measured to be 150 ± 7 HV before the test, was reduced at the die cavity surface nearly to 100 HV after only 330 cycles. In contrast to the X32CrMoV33 hot work tool steel, the entire section of the CuCrZr sample was affected owing to the very high thermal conductivity of this alloy. Hardness of the hot work tool steel, 442 ± 7 HV before the thermal fatigue test, was reported to drop below 300 HV at the front face after 500 cycles [22]. A surface layer 10 mm deep has been adversely affected by thermal exposure since a surface stock of approximately this size had to endure during thermal cycling temperatures above 650 °C where the temper resistance of the hot work tool steels deteriorate [8–10, 29]. It is fair to conclude from the above that the resistance to softening of the CuCrZr alloy is not sufficient to sustain the temperatures thixoforming dies experience during forming operations much like the X32CrMoV33 tool steel. This, however, may not be critical since the magnitude of thermal stresses generated due to thermal cycling, which approximate steel thixoforming are much lower than those obtained with a hot work tool steel die.

What impairs the response to thermal cycling of the CuCrZr alloy samples appears to be the extensive surface degradation due to oxidation. Copper is known to be readily oxidized at high temperatures as its oxide is not protective [30]. Thermal cycling has indeed produced thick oxide scales not only on the heated front face but on the entire sample (Fig. 7). The surface quality of these samples after 300 cycles (Fig. 7b) is judged to be a lot worse than those of hot work tool steel samples in spite of lower thermal cycling temperatures (Fig. 7c) This implies a much more rapid deterioration in the former. TGA tests provide further evidence for the extensive oxidation of the CuCrZr alloy in the temperature range of interest (Fig. 8). The weight gain of the Cu alloy due to oxidation is many times greater than that of the hot work tool steel above 450 °C. These oxide scales eventually start to detach from the surface with continued thermal cycling, due to an apparent thermal expansion mismatch with the underlying metal. The detached oxide scales were shown by XRD to be predominantly Cu_2O, cuprous oxide, with additional weak reflections of the CuO, cupric oxide (Fig. 9). The growth of Cu_2O layers on Cu alloys is followed by further oxidation of Cu_2O to CuO with increasing temperatures owing to an activation energy, which becomes very small at higher temperatures due to the very small thermodynamic driving force and the fast lateral growth of CuO [31].

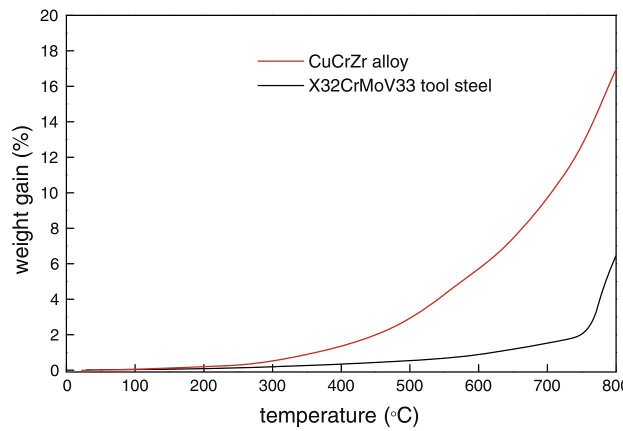

Fig. 8 Weight gain as a function of temperature of the CuCrZr alloy and X32CrMoV33 hot work tool steel

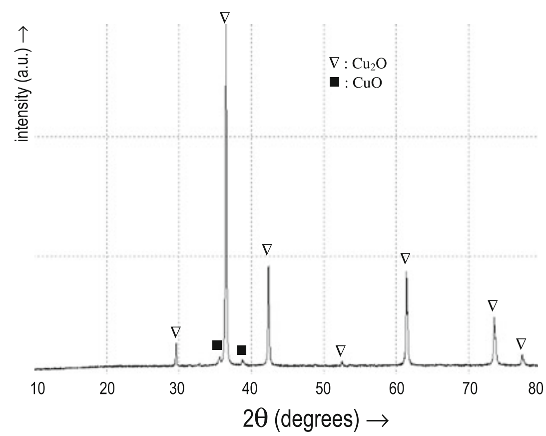

Fig. 9 X-ray diffraction pattern of the surface oxides that form on the CuCrZr alloy sample during thermal cycling

CuCrZr alloy enjoys an exceptional thermal stress state during thermal cycling thanks to a very favourable thermal conductivity. Thermal fatigue cracking does not at all appear to be a limiting factor for this high thermal

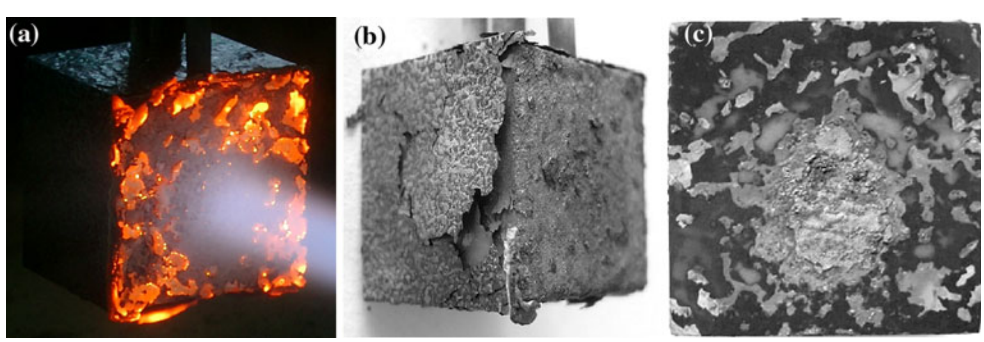

Fig. 7 Front face of the CuCrZr alloy sample **a** during thermal cycling and **b** after 330 cycles and **c** of the X32CrMoV33 hot work tool steel sample after 1500 cycles

conductivity alloy. The temper softening may not be a serious threat to its performance under steel thixoforming conditions either. CuCrZr alloy fails essentially due to severe surface degradation due to high temperature oxidation. This problem could possibly be circumvented if dies manufactured from CuCrZr alloy is coated with a thin hard layer, which could serve as a barrier against oxidation.

Conclusions

Samples of CuCrZr alloys were cycled thermally between 450 ± 10 and 620 ± 10 °C, every 30 ± 1 s. The thermal conductivity of the CuCrZr alloy, nearly an order of magnitude higher with respect to that of the conventional tool steel, proved to be very beneficial in reducing the magnitude of thermal stresses generated at the surface upon thermal cycling. The maximum compressive and tensile stresses produced at the front face of the CuCrZr alloy were estimated to be approximately 30 and 10 MPa, respectively, much smaller than those endured by the conventional tool steel. The very favourable thermal stress state in the case of the CuCrZr alloy was completely negated, however, due to its very inferior resistance to oxidation and temper softening.

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