Temperature effect on strain-induced phase transformation of cobalt

Pierre-Antoine Dubos, Jamal Fajoui, Nadjib Iskounen, Michel Coret, Saurabh Kabra, Joe Kelleher, Baptiste Girault, David Gloaguen

Temperature effect on strain-induced phase transformation of cobalt

DUBOS Pierre-Antoine[a,*], FAJOUI Jamal[a], ISKOUNEN Nadjib[a], CORET Michel[a], KABRA Saurabh[b], KELLEHER Joe[b], GIRAULT Baptiste[a] and GLOAGUEN David[a]

[a] Université de Nantes – Centrale Nantes, Institut de Recherche en Génie Civil et Mécanique (UMR CNRS 6183), Saint-Nazaire, France
[b] ISIS, STFC Rutherford Appleton Laboratory, Chilton Didcot, Oxfordshire, United Kingdom

* Corresponding author: pierre-antoine.dubos@univ-nantes.fr

Abstract

Thermal and mechanical effects on the phase transformation of polycrystalline two-phase HCP/FCC cobalt have been studied in coupled and decoupled ways. This experimental work has involved *in situ* X-ray and neutron diffraction analysis to determine phase proportions under various thermomechanical conditions, those which are not referenced in the litterature. A quantitative analysis is proposed to better understand phase transformation in a cobalt rolled sheet. New experimental results show that the metastable FCC retained phase can be transformed into HCP phase by a mechanical loading. In accordance with the theory and the literature, the prominent phase (HCP) can subsequently be transformed with an increase of temperature above 743 K.

Keywords: Cobalt; phase transformation; diffraction; mechanical behavior; *in situ* characterization.

1. Introduction

High-purity polycrystalline cobalt exhibits an allotropic transformation (reversible and diffusionless) from HCP (Hexagonal-Closed-Packed) phase to FCC (Face Centered-Cubic) structure around 713 K (austenitic transformation). The reverse transformation, from FCC to HCP phase (named martensitic transformation [1]), occurs at roughly 603 K. The cobalt transformation involves a temperature hysteresis which depends on the number of applied thermal transformation cycles [2-3]. However, the cobalt martensitic transformation is incomplete. Consequently, at room temperature, a residual FCC phase stands along with the predominant HCP phase [4].

Previous results exhibited an important improvement of the mechanical properties of cobalt when it presents a two-phase structure [5]. As a result of this knowledge, the literature reports the production, with a vacuum arc apparatus, of two-phase cobalt coatings for medical applications [6].

Sanderson [7] investigated the tensile properties of polycrystalline cobalt at room temperature so as to get the HCP phase stable, using different initial retained FCC phase proportions, grain sizes and sample purities. He has then shown that the retained FCC phase fraction of polycrystalline cobalt, at room temperature, depends on the thermal history, the purity and the grain size. Marx *et al.* [8] studied by X-Ray Diffraction (XRD) the strain-induced phase transformation, at room temperature, in a 2 µm thick film deposited on a polyimide substrate, using *in situ* tensile tests. They have highlighted that the untransformed metastable FCC phase was reduced from 51 % to 8 % when the total macroscopic strain increases from 2 % to 8 %. Straumal *et al.* [9] observed a complete transformation of the FCC phase under severe plastic deformation (high-pressure torsion) in Co-Cu alloys.

The objective of this work is therefore to contribute to the understanding of the influence of mechanical and thermal loadings on the metastable FCC retained phase. First, this study deals with decoupled loading conditions: heating effect followed by a tensile testing at room temperature. In a second step, the thermomechanical coupling is studied. All experiments have focused on the evolution of the FCC phase proportion during *in situ* neutron and X-ray diffraction measurements.

2. Material and methods

The investigated material is a high purity (99.9 at. %) polycrystalline cobalt sheet, cold-rolled down to 0.5 mm in thickness and annealed by GoodFellow society. The as-received material shows two crystallographic phases: moderate temperature HCP and high-temperature metastable FCC, retained at room temperature. Metallographic observations and XRD analyses have revealed an initial grain size of around 25 µm, an initial ratio between the two phases of 75 %HCP/25 %FCC and a quasi-isotropic crystallographic texture.

An *in situ* experiment has been carried out in order to study the influence of temperature on the phase transformation behavior. Variation of FCC and HCP phase composition during heating was monitored by XRD, using Cu anode (with a wavelength $\lambda = 0.1544051$ nm). A θ-2θ scanning mode was used and the diffraction profiles were recorded with 2θ angle ranging from 35° to 95° with a 2θ-step of 0.0157°. The sample was heated between 303 and 773 K at a rate of 0.5 K/s.

In situ tensile tests along rolling direction under neutron diffraction were performed on classical dog-bone shaped samples of $20 \times 7 \times 0.5$ mm^3 in gage volume. They were tested using the ENGIN-X neutron diffraction strain scanning instrument at ISIS facility [10], with a 100 kN Instron testing machine. Measurements were taken at different temperatures (ambient, 623 and 873 K) under various mechanical loads. For each step, the sample was held at an imposed displacement and an initial waiting time was included to obtain a stable load during diffraction measurements and avoid creep phenomena as far as possible. The macroscopic strain was determined using an extensometer that spanned the irradiated region. The Time-Of-Flight (TOF) method allowed us to simultaneously collect, several diffraction peaks from a range of {hk.l} crystallographic planes. A gage volume of $4 \times 4 \times 0.5$ mm^3 including beam divergence was defined by the primary slits and secondary collimator.

The FCC phase volume fraction f^{FCC} was calculated with the method described in [11] and averaged from several groups of family planes: $\{10.0\}_{HCP}$, $\{111\}_{FCC}$, $\{00.2\}_{HCP}$, $\{10.1\}_{HCP}$, $\{200\}_{FCC}$ and $\{10.2\}_{HCP}$.

3. Results and discussion

3.1. Thermal influence

In good accordance with the previous work of Houska *et al*. [3]. The initial f^{HCP} is 73.5 % and the hexagonal phase begins to transform from the austenitic start temperature A_s = 673 K. After a transformation of approximately 1 %/K, the material has an entirely FCC structure. This austenitic transformation is therefore completed at the austenitic finish temperature A_F of 743 K.

3.2. Thermomechanical loading influence

Experimental macroscopic stress-strain curves obtained for tensile tests are plotted in Fig. 1 for the three investigated temperature: 293 K, 623 K (< A_S) and 773 K (> A_F). As noted above, the stress decreases with increasing temperature while ductility increases. The work-hardening rate seems to strongly decrease with temperature. Mechanical properties are more drastically affected when the material is entirely transformed, at 773 K.

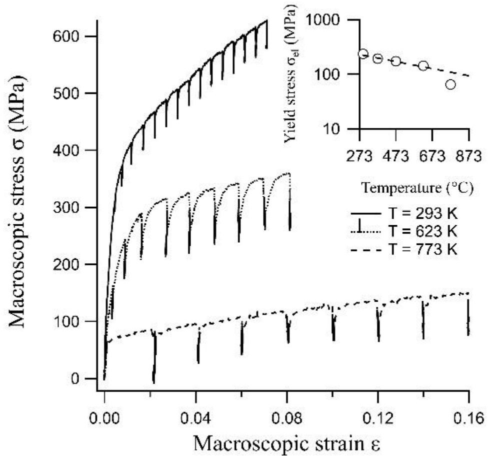

Figure 1. Experimental macroscopic stress-strain curves for various temperatures. Neutron Diffraction analyses were performed after each unloading. The inset gives the temperature effect on the yield stress.

The evolution of the yield stress with temperature, plotted in the inset of Fig. 1, endorses this observation and is consistent with the hardness results reported in literature [12].

In Fig.2, the FCC proportion normalized by its initial value is plotted against the macroscopic (a) stress and (b) strain for tensile tests performed at room temperature, 623 K and 773 K.

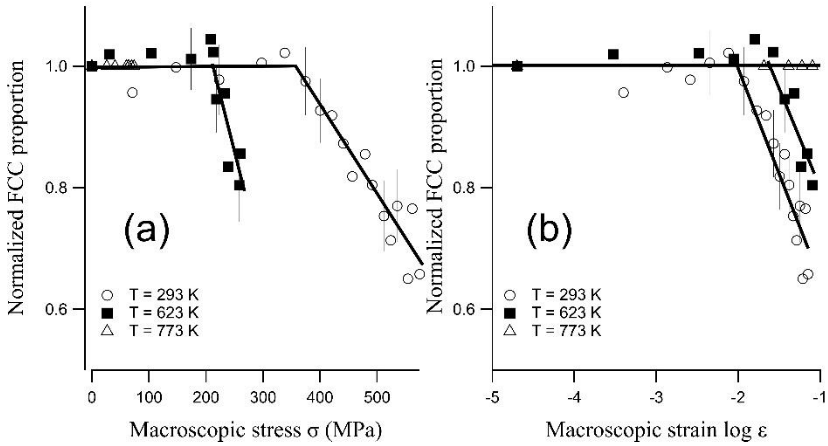

Figure 2. Influence of the temperature on the normalized volume fraction of FCC retained phase evolution during tensile tests plotted as a function of the macroscopic (a) stress and (b) strain.

At room temperature, the FCC phase does not evolve above a deformation of 0.85 %, corresponding to a stress of 1.5 times the yield stress. Beyond, it transforms into HCP phase in a linear proportion to the logarithm of the strain. At the end of the tensile test, a strain level of 7 % has been reached and 35 % of the initial FCC retained phase has been transformed into HCP phase. The transformation rate with strain can be defined by the slope $d[f^{FCC}(\varepsilon)/f^{FCC}(\varepsilon = 0)]/d[\log(\varepsilon)]$ and is equal to -0.48 with an uncertainty of 0.04 at room temperature, as reported in Table 1.

Table 1. Fitting parameters obtained from the figure 2.

	Norm. FCC prop. = -a × σ + b		Norm. FCC prop. = -a × log(ε) + b	
T	293 (K)	623 (K)	293 (K)	623 (K)
$a_{+u(a)}$	1.5×10^{-3} $_{+/-1.3\times10^{-4}}$ (MPa^{-1})	4.0×10^{-3} $_{+/-8.6\times10^{-4}}$ (MPa^{-1})	0.48 $_{+/-0.04}$	0.45 $_{+/-0.08}$
$b_{+u(b)}$	1.5$_{+/-0.06}$	1.9$_{+/-0.20}$	0.01 $_{+/-0.05}$	0.3$_{+/-0.10}$
R^2	0.91	0.81	0.91	0.89
σ_{start}	354 (MPa)	213 (MPa)	-	-
ε_{start}	-	-	8.5×10^{-3}	3.0×10^{-2}

In the case of temperature lower than A_S (i.e. 623 K), the beginning of the FCC-HCP transformation is delayed in term of deformation (around 3.0×10^{-2}). Once started, the FCC proportion decreases in favor of the HCP with a slope equals to -0.45 with an uncertainty of 0.08, as reported in Table 1. Taking into account these uncertainties, the kinetics are similar to those obtained at room temperature. In Fıg. 3, it is shown that temperature lowers the yield strength and seems to have the same effect on the initial transformation stress. This reduction of the stress for the transformation and the modification of the slope at 623 K (Fig. 2. (a) and Table 1), is closely linked to the temperature influence on strain-hardening mechanisms. A temperature rise reduces the work-hardening rate, facilitates the movement of dislocations and leads to an easier phase transformation.

In the case of temperature higher than A_F (i.e. 773 K), the studied sample has a FCC structure, which does not evolve with an increase of the mechanical deformation. The strain-induced FCC to HCP phase is counterbalanced by the thermal effect. At a temperature of 773 K, if a part of the FCC microstructure is transformed into HCP one under the effect of mechanical action, this new HCP phase is instantly retransformed. This effect is thus not detectable with the analysis techniques used. High-energy synchrotron source could be a complementary solution to support these analysis assumptions due to its ultra-fast data acquisition.

Considering that the influence of temperature on the stress required to initiate the transformation is similar to that observed on the yield stress and the ultimate tensile stress, and since the two last values confine the requisite stress value for the transformation initiation. Fig. 3 shows not only that the stress imposed on the material should be large enough to induce the transformation but also that it cannot therefore remain a hypothesis for the non-evolution of the FCC proportion during deformation at 773 K.

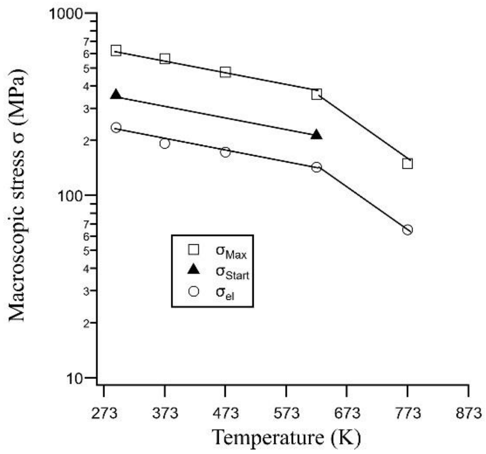

Figure 3. Influence of the temperature on different mechanical properties: yield stress (empty circles), ultimate tensile stress (empty squares) and stress for the initiation of the FCC-HCP transformation (fully triangles)

4. Conclusions

In this research, the following main results and conclusions can be drawn from this new experimental study:

- High-purity polycrystalline rolled sheet presents a two-phase microstructure including metastable high temperature FCC retained phase.
- The majority HCP phase is completely transformed into a FCC phase between 673 K and 743 K.
- The initial FCC retained phase can be transformed by the application of an external mechanical load.
- The initiation of the FCC into HCP phase transformation is delayed in term of deformation for moderate temperature (lower than A_S) but with similar rate to those obtained at room temperature.

- For high temperature (higher than A_F), the competition between FCC-HCP strain-induced transformation and HCP-FCC thermally activated transformation seems to be won over by the effect of temperature.

Acknowledgments

This work is based upon experiments performed at the ENGIN-X instrument at the ISIS Neutron and Muon Source, Didcot, United Kingdom. The authors thank the ISIS neutron Facilities scientific committees for the allocated experimental days (experiment 1910046).

References

[1] Ray A.E., Smith S.R., Scofielf J.D., Study of the phase transformation of cobalt, J. Ph. Equilib., 12, (1991), 644-648. https://doi.org/10.1007/BF02645161

[2] Matsumoto H., Variation in transformation hysteresis in pure cobalt with transformation cycles, J. Alloy. Compd., 223, (1995), L1-L3. https://doi.org/10.1016/0925-8388(95)01523-X

[3] Houska C.R., Averbach B.L., Cohen M., The cobalt transformation, Acta Metall., 8, (1960), 81-87. https://doi.org/10.1016/0001-6160(60)90088-2

[4] Fleurier G., Hug E., Martinez M., Dubos P.A., Keller C., Size effects and Hall–Petch relation in polycrystalline cobalt, Philos. Mag. Lett., 95, (2015), 122-130. https://doi.org/10.1080/09500839.2015.1020351

[5] Bouquet G., Dubois B., Influence of the FCC phase retained at room temperature on the mechanical properties of cobalt, Scr. Metall., 12, (1978), 1079-1081. https://doi.org/10.1016/0036-9748(78)90078-9

[6] Straumal B.B., Gust W., Vershinin N.F., Watanabe T., Igarashi Y., Zhao X. Stable and metastable phases in the vacuum arc deposited Co thim films, Thin Solid Films, 319 (1998), 124-127. https://doi.org/10.1016/S0040-6090(97)01106-1

[7] Sanderson C.C., Deformation of polycrystalline cobalt, PhD thesis, University of British Columbia, 1972.

[8] Marx V.M., Kirchlechner, C., Breitbach B., Cordill M.J., Többens D.M., Waitz T., Dehm G., Strain-induced phase transformation of a Co film on flexible substrates, Acta Mater., 121, (2016), 227-233. https://doi.org/10.1016/j.actamat.2016.09.015

[9] Straumal B.B, Mazilkin A.A., Baretzky B., Schütz G., Rabkin E., Valiev A. Z. Accelerated diffusion and phase transformations in Co-Cu alloys driven by severe plastic deformation, Mater. Trans., 53, (2012), 63-71. https://doi.org/10.2320/matertrans.MD201111

[10] Santisteban J.R., Daymond M. R., James J. A. Edwards L. ENGIN-X: a third-generation neutron strain scanner, J. Appl. Cryst., 39, (2006) 812-825. https://doi.org/10.1107/S0021889806042245

[11] Shang S., Hu G., Shen J. Determination of volume fraction in textured titanium alloy sheet, Scr. Mater., 45, (2001), 287-292. https://doi.org/10.1016/S1359-6462(01)01028-4

[12] Betteridge W., The properties of metallic cobalt, Prog. Mater. Sci., 24, (1979), 51-142. https://doi.org/10.1016/0079-6425(79)90004-5