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Pierre-Antoine Dubos, Jamal Fajoui, Nadjib Iskounen, Michel Coret, Saurabh Kabra, et al.. Neutron and X-ray diffraction measurements to explore the influence of thermal, mechanical and thermomechanical loadings on the FCC retained phase of two phase HCP/FCC cobalt. International Conference on Materials Science, Mechanical and Automotive Engineerings and Technology, Jun 2020, ISTANBUL, Turkey. hal-04295541

HAL Id: hal-04295541

<https://hal.science/hal-04295541>

Submitted on 21 Nov 2023

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Neutron and X-ray diffraction measurements to explore the influence of thermal, mechanical and thermomechanical loadings on the FCC retained phase of two phase HCP/FCC cobalt

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Abstract

Thermal and mechanical effects on the phase transformation of polycrystalline two-phase HCP/FCC cobalt have been studied in a coupled and decoupled way. This experimental work has involved *in situ* X-ray and neutron diffraction analysis to determine phase proportions under various thermomechanical conditions. A quantitative analysis is proposed to better understand phase transformation in a cobalt rolled sheet. Results show that the metastable FCC retained phase can be transformed into HCP phase by a mechanical loading (tensile or stamping). In accordance with the theory and the literature, the prominent phase (HCP) can subsequently be transformed with an increase of temperature above 470 °C.

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

1. Introduction

Among all HCP (Hexagonal Close-Packed) alloys, cobalt is one of the least studied although it is of a prime interest due to its specific mechanical and magnetic properties. Cobalt is also interesting because it exhibits a much higher melting point and a very low stacking fault energy as compared to others HCP metals, giving it very particular deformation mechanisms [1].

High-purity polycrystalline cobalt exhibits an allotropic transformation (reversible and diffusionless) from HCP phase to FCC (Face Centered-Cubic) around 440 °C (austenitic transformation). The reverse transformation, from FCC to HCP phase (named martensitic transformation [2]), occurs roughly at 330 °C. The cobalt transformation involves a temperature hysteresis which depends on the number of applied thermal transformation cycles [3-5]. However, the cobalt martensitic transformation is incomplete. Consequently, at room temperature, a residual FCC phase stands along with the predominant HCP phase [6-7].

Previous results exhibited an important improvement of the mechanical properties of cobalt when it presents a two phase structure [8].

Sanderson [9] 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, grains sizes and purity samples. 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 grains size. Marx et al. [10] 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 %.

The objective of this work is thus 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 either tensile testing or stamping at room temperature. In a second step, the thermomechanical coupling is studied. All experiments have focused on the evolution of FCC phase proportion during *in situ* neutron and X-ray diffraction measurements.

2. Materials and methods

2.1. Material description

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.

2.2. X-ray diffraction measurements

An *in situ* experiment has been carried out in order to study the influence of temperature on phase transformation behavior. Variation of FCC and HCP phase composition during heating was monitored by XRD technique, using Cu anode (CuK_{α1+2} radiation,

wavelength $\lambda = 1.5413 \text{ \AA}$). 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° . A heating of a sample was conducted between 30 and 500°C with a rate of 0.5°C/s . At 18 chosen temperature, diffraction peaks are recorded. A *post mortem* XRD analysis has been performed on a sample strained under biaxial Nakazima test, which is described elsewhere [11-13] and represented in Fig.1.a. In plane macroscopic strain field gradients were measured by Digital Image Correlation technics to evaluate von Mises strain assuming plastic incompressibility. Various position between the top of the dome and blank holder were analyzed in order to investigate the influence of strain gradient on the FCC retained phase proportion.

2.3. Neutron diffraction measurements

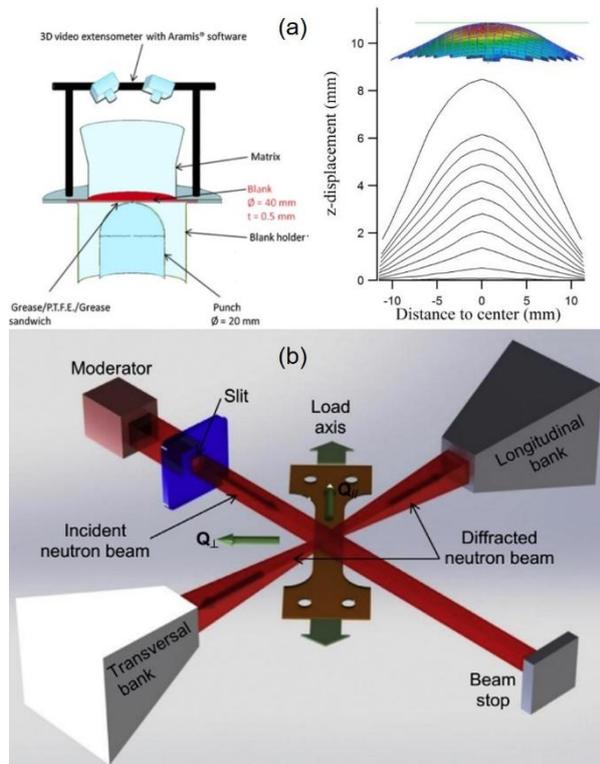


Figure 1. Experimental device for the biaxial stamping test and associated data (a) [11-13]. Schematic view of the set-up used on the neutron diffraction instrument ENGIN-X (b) [14].

In situ tensile tests under neutron diffraction have been achieved on classical dog-bone shaped samples of $20 \times 7 \times 0.5 \text{ mm}^3$ in gage volume. They were tested using the ENGIN-X neutron diffraction strain scanning instrument (Fig.1.b) at ISIS facility, Rutherford Appleton Laboratory (Didcot, UK) with a 50 kN Instron testing machine [15]. Measurements have been achieved at different temperatures (ambient, 350 and 500°C) under various mechanical loads (in an increment force control mode in elasticity, and in an increment displacement control mode in plasticity with a step-by-step displacement dependant of the analysed temperature). For each step, the sample has been hold at an imposed displacement and a waiting time have been imposed to obtain a stable load during diffraction measurements.

The macroscopic strain was determined using an extensometer that spanned the irradiated region. A type K-thermocouple was used to monitor and control the temperature. ENGIN-X instrument presents a horizontal loading axis positioned at 45° to the incident beam. Two detector banks are set up horizontally and at $\pm 90^\circ$ angles to the incident beam, enabling simultaneous measurements of lattice strains in both longitudinal (LD) and transversal (TD) directions as regard to the applied load (Fig.1.b). The Time Of Flight (TOF) method allowed us to collect at the same time, all the $\{hk.l\}$ crystallographic plane families data. A gage volume of $4 \times 4 \times 0.5 \text{ mm}^3$ including beam divergence was defined by the primary and secondary instrument slits.

2.4. Phase proportion quantification

The FCC phase volume fraction f^{FCC} has been determined for each measurement point using the equation (1):

$$f^{FCC} = \left(1 + \frac{I_{hkl}^{HCP} R_{hkl}^{FCC}}{I_{hkl}^{FCC} R_{hkl}^{HCP}} \right)^{-1} \quad (1)$$

where I_{hkl} is the integrated intensity of the corresponding $\{hkl\}$ peak. R_{hkl} is the reflectivity of the lattice plane $\{hkl\}$, given by the following equation (2):

$$R_{hkl} = \frac{1}{v^2} |F_{hkl}|^2 \left(\frac{1 + \cos^2(2\theta)}{\sin^2(2\theta) \cos(\theta)} \right) m \frac{e^{-2M}}{\mu} \quad (2)$$

where v is the volume of the unit cell (in \AA^3), F_{hkl} is the structure factor, 2θ is the Bragg angle, m is the $\{hkl\}$ planes multiplicity factor, μ is the linear absorption coefficient and e^{-2M} is the Debye-Waller factor [16]. The volume fraction of the phases was calculated 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

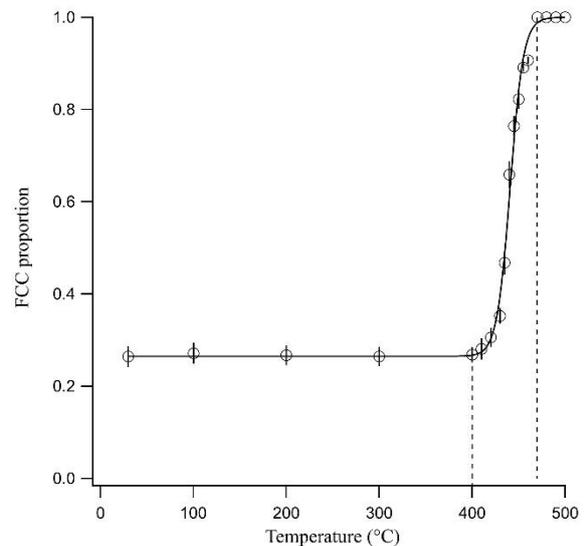


Figure 2. Evolution of the volume fraction of the FCC retained phase during heating between room temperature and 500 °C.

In good accordance with the previous work of Houska et al. [5], Fig. 2. shows the evolution of the volume fraction of the FCC retained phase during a heating between 30 and 500 °C. The initial f^{HCP} is 73.5 % and the hexagonal phase begins to transform from the austenitic start temperature $A_s = 400$ °C. After a transformation of approximately 1 %/°C, the material has an entirely FCC structure. This austenitic transformation is therefore completed at the austenitic finish temperature A_F of 470 °C. To study the thermomechanical response, the temperatures have been chosen lower than A_s and higher than A_F .

3.2. Macroscopic thermomechanical response

Experimental macroscopic stress-strain curves obtained for tensile tests are plotted in Fig. 3 for the three investigated temperature: 25 °C, 350 °C (< A_s) and 500 °C (> 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 500 °C.

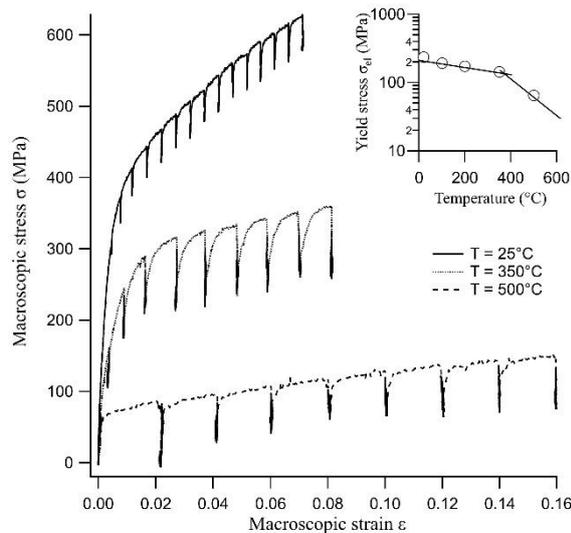


Figure 3. Experimental stress-strain curves for various temperatures. ND analysis are performed after each unloading. The inset gives the temperature effect on the yield stress.

The evolution of the yield stress with temperature, plotted in the inset of Fig. 3, endorses this observation and is consistent with the hardness results reported in the Betteridge review [1].

It can be noted that the phase quantification results performed during these tensile tests (and presented below) are carried out after each mechanical unloading in order to have a stable stress load during the diffraction measurement and avoid creep phenomena as far as possible.

3.3. Mechanical state influence

The most important assets of the biaxial stamping test for the study of strain-induced phase transformation are to allow the access at higher equivalent strain level than a conventional tensile test due to a more important stress triaxiality of the loading, and to obtain on a sole part a strain gradient enabling *post mortem* analysis.

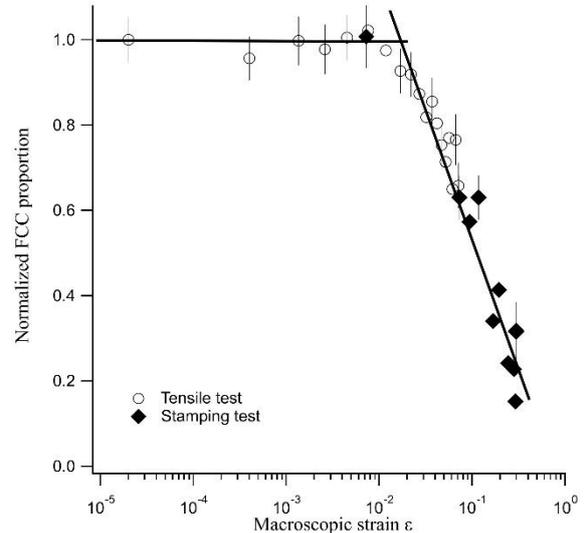


Figure 4. Normalized volume fraction of FCC retained phase during mechanical deformation at room temperature for an uniaxial tensile test and a biaxial stamping test.

In Fig.4., FCC proportion, normalized by its initial value, is plotted against the macroscopic equivalent strain for a tensile test (empty circles) and a stamping test (full lozenges), both performed at room temperature. The FCC phase does not evolve up to a deformation of 0.85 %, corresponding to a stress of 1.5 times the yield stress. Above, it transforms into HCP phase through a linear kinetics with 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 maximum strain level, obtained at the top of the dome of the stamped sample, is equal to 30 % and enables to transform approximately 80 % of the initial FCC retained phase. The transformation rate with strain can be defined by the slope $d[f^{FCC}(\epsilon)/f^{FCC}(\epsilon=0)]/d[\log(\epsilon)]$ 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 5.

	Norm. FCC prop. = $-a \times \sigma + b$		Norm. FCC prop. = $-a \times \log(\epsilon) + b$	
T	20 (°C)	350 (°C)	20 (°C)	350 (°C)
$a_{+u(a)}$	$1.5 \times 10^{-3} \pm 1.3 \times 10^{-4}$ (MPa ⁻¹)	$4.0 \times 10^{-3} \pm 8.6 \times 10^{-4}$ (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} (MPa)	354	213	-	-
ϵ_{start}	-	-	8.5×10^{-3}	3.0×10^{-2}

3.4. Thermomechanical loading influence

In Fig.5., FCC proportion normalized by its initial value is plotted against the macroscopic (a) strain and (b) stress for tensile tests performed at room temperature, 350 °C and 500 °C.

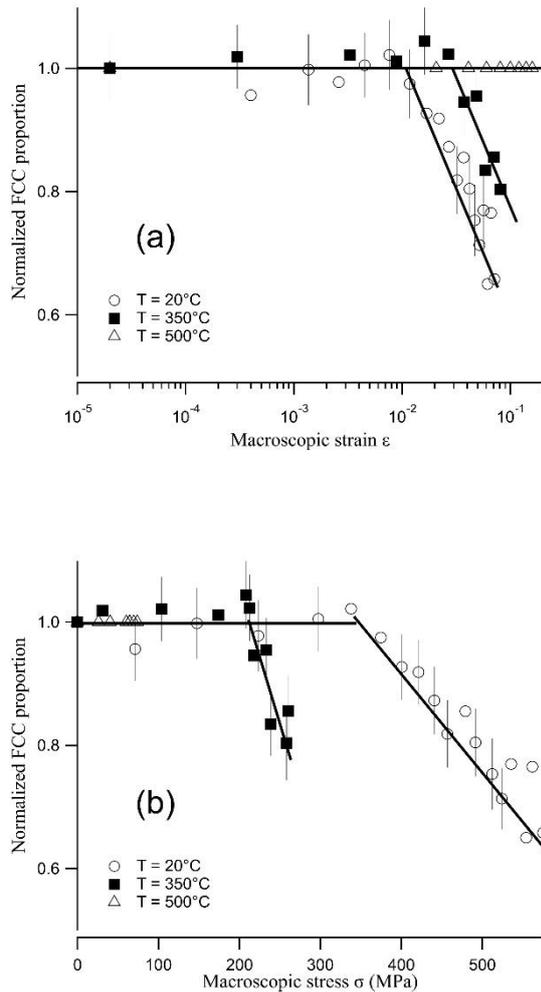


Figure 5. Influence of the temperature on the normalized volume fraction of FCC retained phase evolution during tensile tests plotted as a function of the macroscopic (a) strain and (b) stress.

In the case of temperature lower than A_S (i.e. 350 °C), 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 equal to -0.45 with an uncertainty of 0.08, as reported in Table 1. Tacking into account these uncertainties, the kinetics are almost similar to those obtained at room temperature. In Fig. 6., 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 350 °C (Fig. 5. (b) 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 an easier phase transformation.

In the case of temperature higher than A_F (i.e. 500 °C), 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 500 °C, 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 actually be a suitable 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 to the transformation initiation, Fig. 6. 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 500 °C.

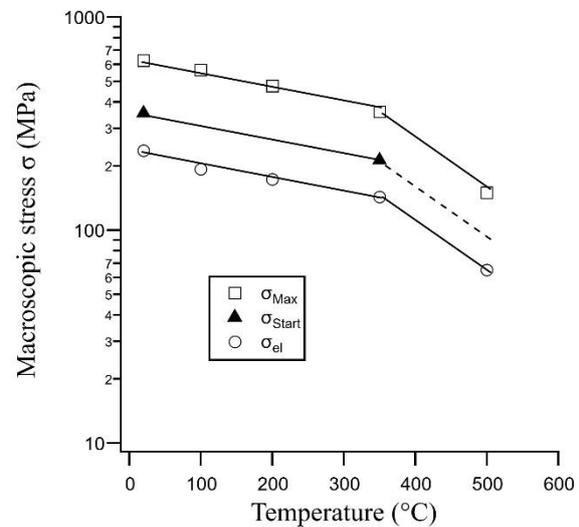


Figure 6. Influence of the temperature on different mechanical properties: yield stress (empty circles), ultimate tensile stress (empty squares) and stress for the initiation of the FCC-HCP transformation (fully triangles)

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 400 °C and 470 °C.
- The initial FCC retained phase can be transformed by the application of a external mechanical load either by tensile test or by stamping.
- The initiation of the FCC into HCP phase transformation is delayed in term of deformation for moderate temperature (lower than A_S) but with kinetics similar 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). The authors also thank E. Hug and N. Barrier, researchers at the CRISMAT laboratory of the University of Caen, France, for the temperature X-Ray diffraction experiments.

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